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Creating Energy Independence

An Energy-Dense Al-NaBH₄-PEMFC Based Power Generator for Unmanned Undersea Vehicles

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Abstract

The main objective of this work is to develop a high-energy density air-independent power generator for UUVs based on a combination of polymer electrolyte membrane fuel cell (PEMFC) with a compact hydrogen generator utilizing Al-NaBH₄ composite fuel. The conditions for the energy-dense and stable storage of NaBH₄ slurries and dense solutions for the extended period of time (6 months and longer) with minimal degradation rate (0.05-0.35% per month) have been determined. The effect of seawater on the kinetics of NaBH₄ and Al-NaBH₄ hydrolysis has been elucidated. Seawater minerals (especially, Mg^{2+}) showed catalytic effect on NaBH₄ hydrolysis. The catalytic effect of Al hydrolysis products on the NaBH₄ hydrolysis was studied. Continuous stable production of a stream of high-purity (99.999%, w/out water vapor) hydrogen by Al-NaBH₄ hydrolysis in water and seawater at the temperature range of 90°C has been demonstrated. A breadboard power generation unit consisting of NaBH₄ delivery system, Al-NaBH₄ hydrolysis reactor and PEMFC has been designed, assembled and performance tested. The unit's performance was comparable to that of PEMFC powered by high-purity H₂ from a tank, which points to the high efficiency of the developed power generation system.

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1. TECHNICAL APPROACH AND JUSTIFICATION

1.1. Future Naval Relevance

Unmanned Undersea Vehicles (UUV) power is one of the militarily critical technologies. Although there have been significant advances in the development of UUV's energy systems/management, it still remains the most challenging and critical area because it limits the overall capability of UUV. Current UUV missions are limited to few days due to the storage limitations of batteries used for propulsion. Modern and future UUVs require much longer endurance: from weeks to months. It is recognized that currently available technology will not meet Navy UUV power requirements, thus, the development of innovative beyond battery-only technological capabilities would be necessary. The main objective of the proposed work is to develop an innovative high-energy density air-independent power generator based on a combination of low-temperature polymer electrolyte membrane fuel cell and a hydrogen generator utilizing composite Al-$NaBH_4$ fuel and seawater for production of hydrogen. The preliminary estimates based on bench-scale experiments indicate that it could potentially meet Navy UUV performance targets of power density.

1.2. S&T Objectives

- Development and breadboard validation of an energy-dense onboard power generation unit consisting of a compact seawater-based H_2 generator integrated with polymer electrolyte membrane fuel cell (PEMFC).
- Targeted operating conditions of the H_2 generator: T=80-90°C; P=1 atm; startup time <1 min; H_2 purity 99.999% (not accounting for water vapor); up to 78% of H_2 to be derived from seawater; no catalysts to be used; no gaseous byproducts, no toxic products to be produced.
- Targeted energy density of the integrated power generation unit in the relevant environment: 0.9 kWh/L (including fuel storage, H_2 generator, PEMFC and BOP).

1.3. Approach

The technical approach is based on the integration of two high-energy density devices: a seawater-based hydrogen generator and PEMFC power plant. In the H_2 generator, two highly energetic (but chemically stable) materials: aluminum and sodium borohydride ($NaBH_4$) synergistically react with water/seawater at 80°C-90°C producing a stream of high-purity humidified H_2 – an ideal fuel for PEMFC, which advantageously operates at the same temperature range. Both Al and $NaBH_4$ have very high volumetric hydrogen generation capacities (assuming water is available) - far exceeding that of other H_2-generating systems.

2. SUMMARY

- Energy density of NaBH$_4$ storage systems as a function of the NaBH$_4$ dilution factor for different storage options: powders/tablets, gels, slurries, and dense solutions were determined and analyzed from the viewpoint of onboard hydrogen storage/production.

- Solid-state storage of Al-NaBH$_4$ reagents in the form of composite tablets was investigated. The experiments indicated that no degradation of the Al-NaBH$_4$ tablets occurred during 3 months of storage in dry atmosphere, and practically theoretical amount of H$_2$ (close to 100%) could be recovered from the tablet through the hydrolysis reaction in water at 80-90°C.

- NaBH$_4$ storage in the form of gel was studied. Gels were formed by adding gelling polymer in the amount of 1-4 wt% to the stabilized NaBH$_4$ slurry/solution. The amount of H$_2$ recovered from NaBH$_4$ gel stored over 3 months period was close to the theoretical amount of hydrogen contained in NaBH$_4$ (within the margin of experimental error of 5%).

- Al gel was produced by adding gelling polymer in the amount of 1-2 wt% to Al:H$_2$O (1:2 wt) system. Long-duration storage experiments showed, however, that Al gel substantially hardened over time (weeks) and became too thick to be transportable by syringe pump. Although no hydrogen was produced during the storage, in all likelihood, there was some form of interaction between Al powder and gelling polymer which resulted in hardening of the gel.

- Experimental studies involving NaBH$_4$ storage in the form of NaOH-stabilized slurries and dense solutions were conducted. The results indicated that the long-term stability of the NaBH$_4$ slurries could be improved by increasing the NaBH$_4$ content of the slurries and/or the amount of added alkaline stabilizer. The slurries with NaBH$_4$:H$_2$O ratios in the range of 1:1.8 to 1:2 (wt) showed adequate long-term stability properties. It was found that in most cases, over 6 months storage period, the NaBH$_4$ degradation rate was below 1% and hydrogen recovery rate exceeded 95%, and practically all hydrogen in the system was accounted for.

- The hydrogen balance of the studied NaBH$_4$ slurries was determined in order to verify that no side reactions involving NaBH$_4$ degradation occurred during long-duration tests. It was demonstrated that in most cases, the hydrogen balance reached about 95%. Considering the experimental margin of error of 5%, this fact evidences that no side reaction involving NaBH$_4$ degradation occurs in the system during long-term tests.

- The testing of different organic stabilizers/carriers for NaBH$_4$ has been conducted. It was found that the NaBH$_4$ slurries based on tetraethyleneglycol dimethyl ether (Tetra-EGDME) had relatively good long-term stability: NaBH$_4$ self-hydrolysis yield of 2.1% over period of 7 months. The slurry with other tested stabilizer: triethyleneglycol dimethyl ether (Tri-EGDME), although, being compatible with SB, did not show good long-term stability.

- The experiments indicated that the combination of two hydrides (NaBH$_4$ and KBH$_4$) in the presence of NaOH stabilizer resulted in the increase in mechanical and chemical stability of the slurries. Most likely, this is due to slightly greater density of KBH$_4$ compared to NaBH$_4$ which enables better match in the density of solid and liquid phases in the NaBH$_4$ slurry.

- A new method of formation and stabilization of the NaBH$_4$ slurries and dense solutions has been developed. The method is based on ultrasonication (>20 kHz) of the NaBH$_4$

slurries and dense solutions for the short period of time (5-15 min). This allowed producing uniform slurries with lesser amount of the alkaline stabilizer (by about factor two). The ultrasonication process did not impact the long-term stability of the slurries.

- Tests on the effect of different materials: stainless steel (SS), polyethylene (PE), polycarbonate, copper, brass, on the long-term stability of $NaBH_4$ slurries were conducted. It was found that the stabilized $NaBH_4:H_2O=1:1.5$ wt. slurry that was in contact with stainless steel and PE over period of 8 months resulted in $NaBH_4$ self-hydrolysis yields of 0.3% and 0.6% (of theoretical amount of H_2), respectively. This demonstrates that both SS and PE can be used as construction materials for $NaBH_4$ storage tanks.

- The effect of seawater on the kinetics of $NaBH_4$ and $Al-NaBH_4$ hydrolysis was determined. It was found that that seawater has a marked effect on $NaBH_4$ hydrolysis. Among seawater minerals, $NaCl$ and Na_2SO_4 showed a negligible effect on the kinetics of $NaBH_4$ hydrolysis, whereas, $MgCl_2$ had a significant accelerating effect on the hydrolysis reaction. The experiments demonstrated that seawater does not significantly affect the kinetics of synergistic $Al-NaBH_4$ hydrolysis at elevated temperatures of 80-90°C. Within the margin of experimental error, the amount of H_2 produced from the reacting system is equal to stoichiometric amount of H_2.

- The catalytic effect of the products of Al hydrolysis (e.g., Al oxide and hydroxide) on $NaBH_4$ hydrolysis was elucidated. The experiments indicated that Al_2O_3 does not exert noticeable catalytic effect on $NaBH_4$ hydrolysis. Although, Al hydroxide shows some catalytic activity, the rate of H_2 production is rather low, and it cannot explain the significant increase in $NaBH_4$ hydrolysis in the presence of Al powder. Thus, most of the catalytic effect of Al reagent on $NaBH_4$ hydrolysis can be attributed to metallic Al, rather than products of its hydrolysis.

- A series of experiments on continuous production of hydrogen by $Al-NaBH_4$ hydrolysis using glass and stainless steel reactors at the range of temperatures 80-92°C were conducted. Due to the exothermic nature of the $Al-NaBH_4$ hydrolysis reaction, the temperature regime in the reactor has to be carefully maintained within $\pm 2°C$ during the experiment. A continuous stable production of a hydrogen stream with purity of 99.999 v.% (w/out water vapor) from $NaBH_4$ dense solution (1:2 wt) delivered to the hydrolysis reactor by a syringe pump was demonstrated. The experiments demonstrated that H_2 flow from the reactor can be regulated by varying two parameters: the rate of $NaBH_4$ delivery and temperature. In general, the H_2 production rates tend to be more stable at the higher level of temperature (e.g., 90°C, compared to 80°C).

- The performance-testing of PEMFC integrated with the hydrogen generator was carried out. The stream of hydrogen produced by the H_2 generator was of required purity for the optimal operation of PEMFC. The unit performance was identical to that of PEMFC fueled by commercial high-purity H_2 (from a tank), which points to the high efficiency of the developed power generation system. The energy efficiency of the PEMFC was estimated at 40-45%.

3. TECHNICAL BACKGROUND

3.1. Overview of On-board Power Generators for UUV Application

Naval UUVs require high-energy density storage and propulsion system that enables high speed and endurance combined with a stealth operation. The Navy has established several general classes of UUVs to encompass all the possible applications. The power source selection depends primarily on the speed and endurance requirements for a particular class of a vehicle [1,2]. Air-Independent Propulsion (AIP) systems are desirable to avoid resurfacing for several hours at a time, but the weight and volume of oxidant storage on board must be accounted for [2,3]. The UUV must also be neutrally buoyant, start up rapidly, and be capable of quick, easy and safe refueling at sea [1-4]. The following is a brief analysis of capabilities of existing and emerging UUV energy systems.

Batteries. The advantages of batteries are that they are compact and can fit most shapes, but they have a high initial cost and relatively short range. Rechargeable batteries are less expensive over life-time, but the recharging docks and other support equipment can present significant cost. Also, replenishing at sea is slow and can be unsafe. The majority of early UUV systems were equipped with Lead Acid batteries. Some UUV designs included Silver-Zinc batteries, but the cost was prohibitive [5]. Recent advances in NiMH batteries fostered their wide-spread application in current UUVs. Aluminum – Oxygen cell was introduced by DARPA, which allowed significantly increasing the endurance of UUVs. Lithium is commonly used in battery technology because it is the lightest metal, so higher energy densities are possible [1]. Although different types of batteries involving lithium, e.g., primary (Li-SOCl$_2$) and rechargeable (Li-ion, Li-polymer) batteries, potentially have a high power density, none of these options are expected to be able to meet Navy future energy density goals for UUVs [2-4]. Hybrid systems have also been proposed, in which a Li-based rechargeable battery is usually paired with a primary power source. The battery is used for rapid start-up and peak power generation, and is recharged by the primary power loop as needed.

Fuel Cells (FC). Recent advances in FC technology make them potentially suitable as a power source for UUV. FCs operate without moving parts and have a higher energy density than most types of batteries (see Table 1) [1,3]. They are also safer and permit extended mission durations compared to battery power sources [3,6]. In principle, two types of FC: low- and high-temperature FC can be utilized in UUVs.

Table 1 - Fuel Cell vs. Battery Performance [1,3]

Type of System	Specific Energy, Wh/kg	Energy Density, Wh/L	Max Mission at 2.5 kW, hr	Number of cycles
Ni-Cd	30	75	3	1500
Lead Acid	30	65-95	3	> 300
NiMH	95	330	8	500
AgO-Zn	110	240	9	15
Li-Ion	130	325	11	~2000
Li Polymer	210	330	18	> 600
Li-SOCl$_2$	~ 450	900-1000	35-38	1
PEM (NaBH$_4$ + LOX)	330	340	21	150
SOFC (C$_{12}$H$_{26}$ + LOX)	400-450	400-450	30-40	30 (??)

Polymer electrolyte membrane FC (PEMFC) operate at relatively low temperatures (<90°C) and has the potential to meet the Navy most critical objectives: power density, rapid startup, endurance, and stealth. The major shortcoming of PEMFC is that it is very sensitive to some impurities in hydrogen fuel (e.g., CO, H_2S, NH_3) that could easily poison Pt-based catalyst commonly used in PEMFC.

Solid Oxide Fuel Cells (SOFC) operate at much higher temperatures (700-1000°C) and can use a variety of gaseous and liquid fuels that could be externally or internally reformed on board. Impurities such as carbon monoxide (CO) are tolerated, but the startup time is long (15-30 minutes) due to the high operating temperature [3]. Moreover, a fuel reformer, scrubbers, CO_2 containment devices, heat exchangers, cooling loops, and other auxiliary equipment (balance of plant, BOP), add substantially to the system volume and therefore lower the overall energy/power density [3,4]. Waste heat from the SOFC can be used for the endothermic steam reforming process in a closed cycle, but careful thermal management is required to prevent the system from overheating [3]. Although, SOFC technology looks promising for UUV applications, major technical challenges have to be overcome, including: SOFC reliability and long-term mechanical stability issues, long start-up times, CO_2 scrubber efficiency, fuel recycling, high BOP parasitic power requirements, and others.

Fuel Storage Options. One of the major considerations for FC applications is fuel selection. Liquid fuels typically have a high energy density, and make refueling at sea fast and simple [1,2]. However, the energy density is reduced by the need for an on-board reformer and other supporting equipment. Fuel reformers based on steam reforming (SR), partial oxidation (POX) or autothermal reforming (ATR) processes are well-established, low risk technologies [1,2,4]. These processes, however, operate at high temperatures and generate carbon dioxide (CO_2) that must be contained on board for the duration of the mission. Liquid fueled systems, with the exception of pure liquid hydrogen (LH_2), are very complex technological devices with long start-up times due to higher temperatures required [1,4].

Since PEMFC require high purity hydrogen (H_2), impurities such as H_2S and carbon monoxide (CO) that are typical of hydrocarbon reformate must be completely removed to avoid equipment and performance degradation which adds to the complexity of the system. As a result, it is more practical to use hydrogen storage techniques that do not involve such impurities, e.g., pure liquid H_2, reversible metal hydrides, or chemical hydrides.

The use of reversible metal hydrides is expensive, but reduces the weight/volume of the fueling system compared to high pressure or cryogenic storage, and improves PEMFC performance compared to hydrocarbon reformate. Metal hydrides have been researched for decades as H_2 storage materials, however, their hydrogen capacity is still limited to 2-3 wt%. The H_2 is released from metal hydrides under lower pressure and elevated temperatures to meet engine fuel demands, but the required H_2 desorption temperatures (well above 100°C) often exceed the PEMFC operating temperature. Even at higher temperatures, metal hydrides do not entirely desorb the stored hydrogen, so the cycle efficiency can be quite low. The desorption kinetics are slow due to atomic diffusion, and the materials are subject to cyclic fatigue and gradual degradation [6].

Chemical hydrides irreversibly release essentially pure H_2 by either thermolysis or hydrolysis reactions [6]. The examples of chemical hydrides include sodium borohydride, ammonia borane, and others. $NaBH_4$ catalytic hydrolysis has been described extensively in the literature, with activation energies ranging from 19-67 kJ/mol depending on the concentration of

NaBH4, the catalyst used, the presence of a stabilizer, and the temperature range investigated [7]. The shortcomings of NaBH4 based systems are that NaBH4 is used in the form of dilute alkaline solutions, and catalysts must be used to extract hydrogen. Expensive noble and transition metals and their salts are typically used as catalysts, including platinum (Pt), palladium (Pd), ruthenium (Ru), cobalt (Co), and nickel (Ni).

3.2. Technical Approach

The proposed technical approach is based on the integration of two high-energy density devices: a seawater-based hydrogen generator and PEMFC power plant. In the H_2 generator, two highly energetic (but chemically stable) materials: aluminum and sodium borohydride (NaBH4) synergistically react with water/seawater at 80°C-90°C producing a stream of high-purity humidified H_2 – an ideal fuel for PEMFC, which advantageously operates at the same temperature range. Both Al and NaBH4 have very high volumetric hydrogen generation capacity (assuming water is available): 10 and 7.5 $kW_{th}h/L$, respectively - far exceeding that of other H_2-generating systems.

Another advantage of the proposed composite fuel is that both Al and NaBH4 are thermally and chemically stable: individually, they do not (or very slowly, without catalysts) react with water at ambient conditions. This allows their safe on-board storage and handling during refueling operations. The phenomenon of synergistic hydrolysis of Al and NaBH4 with production of pure hydrogen has been discovered at UCF (two patents granted: US Patent 8,273,140 and 7,803,349). In particular, it was found that in the presence of each other Al and NaBH4 energetically, but controllably, produce H_2 from water (or seawater) on demand: Al acts as catalyst for NaBH4 hydrolysis, and NaBH4 (and its hydrolysis products) removes the protecting oxide layer from Al surface facilitating its reaction with water at ambient temperature (hence, the synergistic action). Fig. 1 depicts the schematic of the synergistic action of the three-way Al-NaBH4-H_2O system: H_2 is efficiently generated when all three components are simultaneously present in an optimal molar ratio.
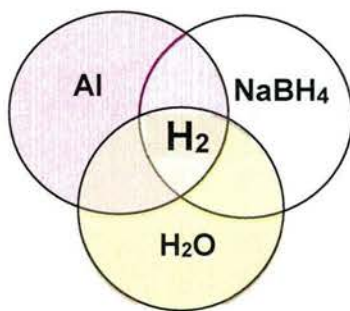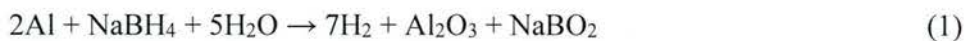

Fig. 1. Schematic diagram of synergistic hydrolysis of Al-NaBH4

The overall reaction stoichiometry can be presented (in a simplified generic form) as follows:

$$2Al + NaBH_4 + 5H_2O \rightarrow 7H_2 + Al_2O_3 + NaBO_2 \tag{1}$$

Note that 5 moles of H_2 out of 7 moles of H_2 (or 71%) are derived from water (or seawater). The

Figure 2 depicts the simplified schematic diagram of the proposed power generation unit for UUV propulsion.
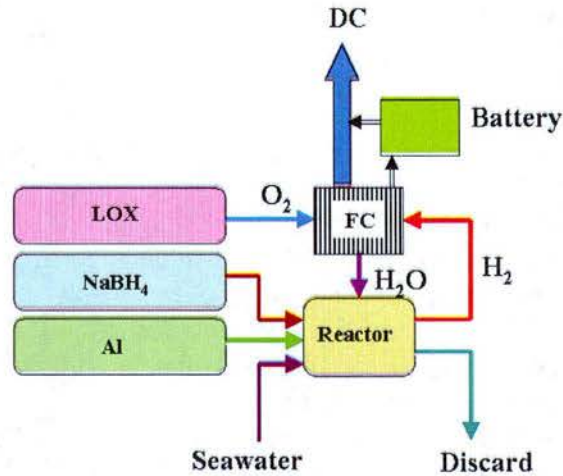

Fig. 2. Schematic of the proposed integrated power generation unit for UUV propulsion

The UUV energy section consists of a hydrogen generator (a hydrolysis reactor), PEMFC, an auxiliary Li-ion battery (for startup, peak loads, etc), Al, NaBH₄ and liquid oxygen storage tanks (other options for oxidant storage can also be considered). The source of water for the hydrolysis reaction is (preferably) filtered seawater, supplemented with pure water produced by PEMFC. The hydrolysis reactor is equipped with a means of reagents delivery such that the rate of hydrogen production can be precisely and reliably controlled. The hydrolysis reaction products (aluminum oxide/hydroxide, sodium metaborate) are non-toxic and environmentally benign compounds: they can be discarded without any harm to marine biota (alternatively, they can be stored on board in a bladder type system).

For the estimation of the UUV energy section volume and energy density of the power generator the following input data (assuming the Navy UUV objective metrics [8]) are used: energy produced 1800 kWh, mission duration 70 days.

4. TECHNICAL SECTION

4.1. Assessment of On-board Storage Options for Al and NaBH4

Fig. 3 summarizes different storage options for Al and $NaBH_4$ on-board UUV: solid (powders, tablets) quasi-liquid (gels) and liquid (slurries and dense solutions). The parameters include:
- feasibility of storage
- energy density of the system
- stability (both chemical and mechanical)
- transportability (from a storage vessel to a hydrolysis reactor)

Storage option	Al	NaBH$_4$	Energy density	Stability*	Transpor-tability
Powders	🟢	🟢	🟢	🟢	🔴
Slurries	🔴	🟢	🟢	🟢	🟡
Gels	🟢	🟢	🟢	🟢 #	🟡
Dense solutions	🔴	🟢	🟡	🟢	🟢

🟢 Feasible/Good
🟡 Satisfactory
🔴 Not feasible

*Stabilized systems
NaBH$_4$ gels

Fig. 3. Different storage options for Al and NaBH$_4$ on-board UUV

It is evident that $NaBH_4$ could be stored on-board UUV in the form of powders, slurries, gels and dense solutions, whereas, Al can only be stored in the form of powders and gels. Transportability of powders can be problematic. It is clear that neither of the storage options can meet all criteria, thus, trade-offs would be necessary.

Fig. 4 quantitatively compares different $NaBH_4$ on-board storage options. The storage system energy density as a function of the $NaBH_4$ dilution factor for such storage options as powders/tablets, gels, slurries and dense solutions are shown on the diagram. For the comparison, the energy density data for $NaBH_4$ solutions (10-25 wt%) used in traditional catalytic systems are also included in the Fig. 4. Dense solutions are defined as storage

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systems on the borderline of slurries and physical solubility of NaBH₄ in aqueous solutions at given temperature. The area circled by a blue ellipse is the area of interest to this project.
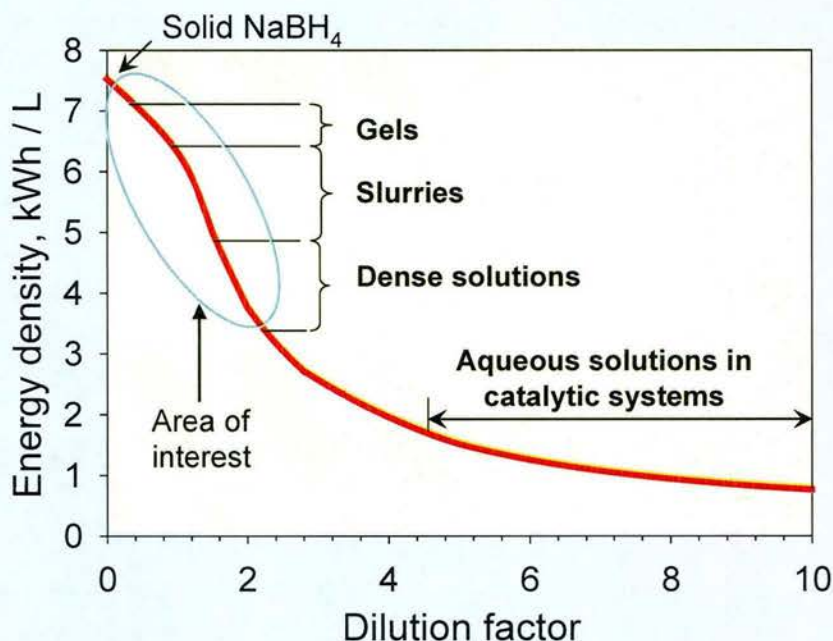

Fig. 4. Summary of onboard NaBH₄ storage options.
Energy density vs NaBH₄ dilution factor.

4.2. Solid-state Storage of Al-NaBH₄ Reagents in the Form of Tablets

As seen in Fig. 4, the storage of Al-NaBH₄ reagents in solid form potentially provides the highest energy density. During the reporting period we continued experimenting with production and testing of tablets made of the mixture of Al and NaBH₄ powders. Al and NaBH₄ powders were carefully mixed (in 1:2 weight ratio) in dry atmosphere to produce a uniform blend, and pressed (5000 psi) into tablets (Fig. 5 A). Each tablet weighed about 0.55-0.65g. The estimated energy density of the tablets was 9-9.5 kWh/L (based on volumetric H_2 capacity of the tablets and lower heating value of H_2). The hydrolysis reaction can be expressed by the equation (1).

The tablets were placed in the vials attached to H_2 measuring system. The tablets were kept undisturbed in dry conditions for 3 months at room temperature, during which no appreciable H_2 production or any other signs of the tablets' degradation were observed. After the prolonged storage, the tablets were tested for the extent of reagents degradation and hydrogen recovery (Fig. 5B). Particularly, in one test, a tablet weighing 0.55 g was transported to a flask where it reacted with water and the amount of released hydrogen was accurately measured. The kinetics of H_2 evolution from hydrolysis of Al-NaBH₄ tablet is shown in Fig. 6.
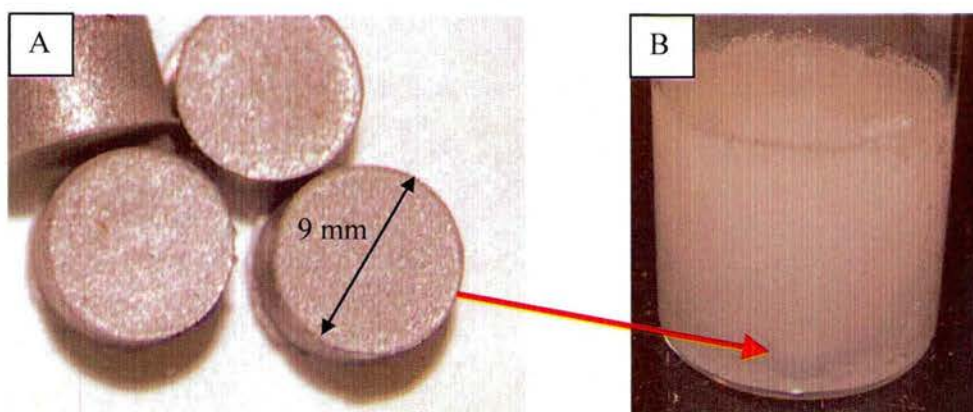
Fig. 5. Al-NaBH$_4$ tablets used for production of pure hydrogen from water.
A- Tablets Al:NaBH$_4$=1:2 (by wt). Tablets weigh 0.55-0.65 g.
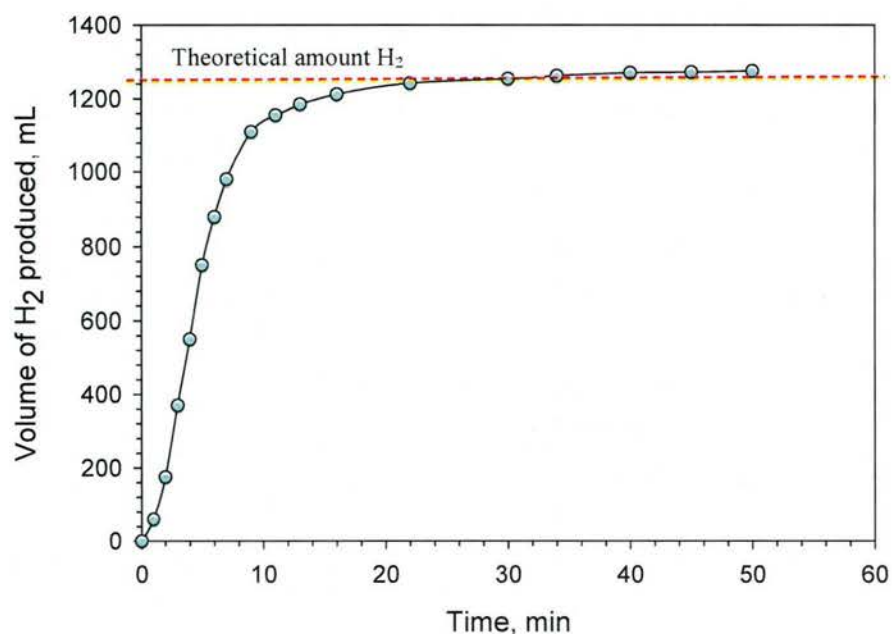B- a tablet reacts with water after 3 months storage.

Fig. 6. Kinetic curve of H$_2$ production from a tablet weighing 0.55g reacting with water at 95°C. The tablet was kept in dry atmosphere for about 3 months before hydrolysis reaction.

The experiments indicated that no degradation of the Al-NaBH$_4$ tablet occurred during 3 months of storage in dry atmosphere, and practically entire stoichiometric amount of H$_2$ (close to 100%) could be recovered from the tablet through the hydrolysis reaction in pure water.

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4.3 Storage of NaBH₄ and Al in Gel Form

NaBH$_4$ and Al powders were mixed with small amounts (1-4% by weight) of a gelling polymer and water to produce a gel. The energy density of the gel-stabilized NaBH$_4$ can be as high as 6.5-7 kWh/L (based on volumetric hydrogen capacity). Fig. 7 A depicts a gel produced by mixing 2% wt. of gelling polymer with distilled water. Fig. 7 B shows a gel produced by adding the gelling polymer in the amount of 3.5 wt% to the NaOH-stabilized NaBH$_4$:H$_2$O (1:1.5 wt) mixture. The gel represents a white uniform slush with the consistency of yogurt.
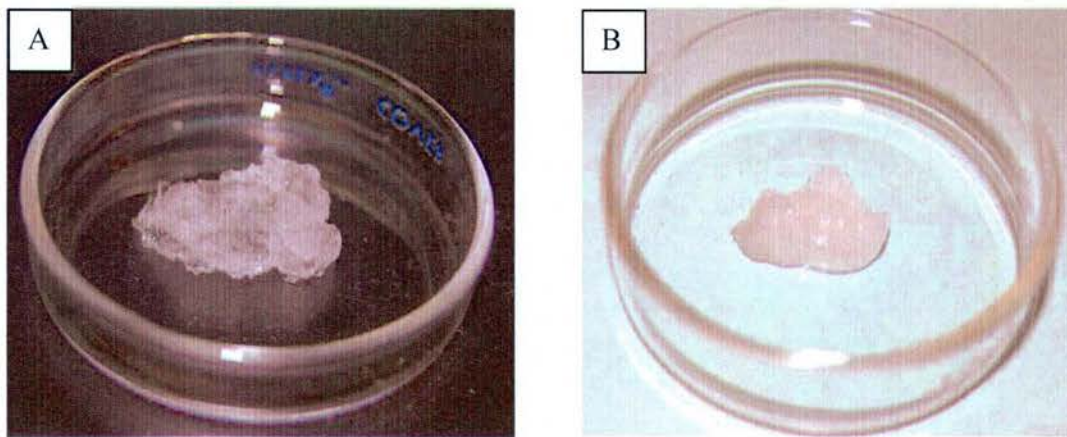

Fig. 7. NaBH$_4$ storage in gel form. A- a gel produced by adding 2% wt. of gelling polymer to deionized water. B- NaBH$_4$ gel produced by adding 3.5% wt. of gelling polymer to stabilized NaBH$_4$:H$_2$O=1:1.5 (wt) solution.

The gel was placed in a glass vial, connected to H$_2$ measuring system and left undisturbed at room temperature for about 3 months. The amount of H$_2$ released from the NaBH$_4$ gel during storage was 1.2 mL, which corresponds to 0.095% of theoretical amount of hydrogen that can be released from NaBH$_4$ hydrolysis. After 3 months storage, the NaBH$_4$ gel was transferred to a flask where it was subjected to acid-hydrolysis to release all available hydrogen from NaBH$_4$. It was found that within the margin of experimental error of 5%, the amount of released H$_2$ was equal to theoretical amount of hydrogen (close to 100%) contained in NaBH$_4$. These experiments indicate that NaBH$_4$ can be efficiently stored for several months in the form of gels with practically no degradation.

We also conducted experiments with Al storage in gel form by mixing Al powder with gelling polymer (1-2 wt%) and adding water. Fig. 8 depicts Al gel produced by adding gelling polymer in the amount of 1 wt% to Al:H$_2$O (1:2 wt) system. The resulting gel represented a medium-to-thick paste, which was suitable for the delivery by a syringe.

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Fig. 8. Al gel produced by adding gelling polymer (1 wt%) to Al:H_2O (1:2 wt) system.

Long-duration storage experiments showed, however, that Al gel substantially hardened over time (2-3 weeks) and became too thick to be transportable by a syringe pump. Although no hydrogen was produced during the storage, in all likelihood, there was some form of interaction between Al powder and gelling polymer which resulted in hardening of the gel (the nature of this interaction is yet to be understood).

4.4 Long-term NaBH₄ Storage in the Form of Slurries

We investigated NaBH₄ storage in the form of slurries for extended period of time (up to 9 months). All experiments were conducted in glass vials, unless otherwise indicated. All samples were kept undisturbed at room temperature ($25\pm1°C$) for the entire duration (4-9 months) of the experiment. Amount of hydrogen released during the NaBH₄ storage experiment was measured with the accuracy of 0.1 mL (which is equal to 0.008% of the amount of hydrogen recoverable from the NaBH₄ samples). At the end of the storage experiments, unconverted NaBH₄ was subjected to acidic hydrolysis (0.01M HCl), during which all remaining hydrogen from NaBH₄ was released.

The hydrogen balance of the studied NaBH₄ slurries was determined in order to verify that no side reactions involving NaBH₄ degradation occurred during long-duration tests. The hydrogen balance takes into consideration the amount of H_2 released during self-hydrolysis over extended period of time (6-8 months) and the amount of H_2 formed during complete ("forced") acid hydrolysis of the slurries at the end of the test. The sum of these two values was correlated with the theoretical amount of H_2 to be released from the slurry (based on NaBH₄ hydrolysis stoichiometry). If no side reactions involving NaBH₄ degradation occurs, then the following balance should be observed:

Total H₂-releasing potential of NaBH₄ = H₂ released during self-hydrolysis + H₂ released by acid hydrolysis

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Quantitatively, the $NaBH_4$ degradation rate (DR), hydrogen recovery rate (HRR) and hydrogen balance (HB) of the system were determined by the following formulae:

$$DR = \frac{H_2^{SH}}{H_2^{Theor.}} \cdot 100\% \tag{2}$$

$$HRR = \frac{H_2^{AH}}{H_2^{Theor.}} \cdot 100\% \tag{3}$$

$$HB = \frac{H_2^{SH} + H_2^{AH}}{H_2^{Theor.}} \cdot 100\% \tag{4}$$

where:
DR is $NaBH_4$ degradation rate over duration of the experiment,
HRR is hydrogen recovery rate after the $NaBH_4$ storage experiment,
HB is hydrogen balance of the system.
H_2^{SH} is the amount of H_2 released through $NaBH_4$ self-hydrolysis over entire test duration.
H_2^{AH} is the amount of H_2 produced by complete acid hydrolysis of $NaBH_4$ slurry at the end of the test.
$H_2^{Theor.}$ is the theoretical amount of H_2 produced by $NaBH_4$ according to the stoichiometry of the $NaBH_4$ hydrolysis reaction.

4.5. Effect of Amount of Water on Kinetics of SB Self-hydrolysis.

We studied the effect of water content of the $NaBH_4$ slurries on their long-term stability (without stabilizers). The kinetics of $NaBH_4$ self-hydrolysis in the slurries with different $NaBH_4:H_2O$ weight ratios of 1:1, 1:1.2, 1:1.4, 1:1.5, 1:1.7, 1:2 and 1:10 was investigated. The results are shown in Fig. 9.
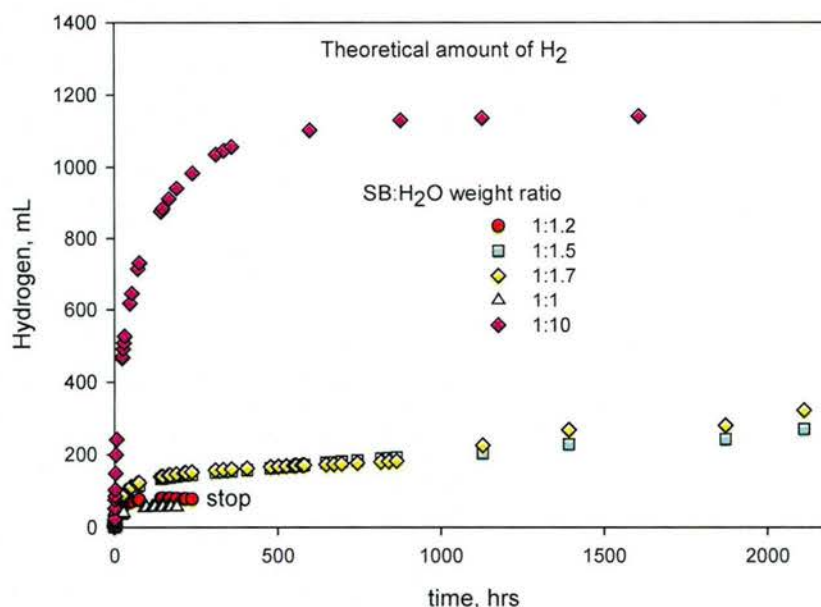
Fig. 9. Effect of $NaBH_4$:H_2O ratio on the long-term stability of the slurries maintained at room temperature. SB is sodium borohydride, $NaBH_4$

Experiments indicated that the water content of the $NaBH_4$-H_2O slurries significantly affected the kinetics of $NaBH_4$ self-hydrolysis and long-term stability of the slurries. The slurries with relatively small amounts of water (e.g., with $NaBH_4$:H_2O ratios of 1:1 and 1:1.2) stopped producing H_2 at the $NaBH_4$ hydrolysis yield of 3.9% and 5.9%, respectively. The slurries with higher content of water, e.g., with $NaBH_4$:H_2O ratios of 1:1.5 and 1:1.7 continued releasing H_2, although at very slow rate (about 0.15 mL/hr H_2), with the $NaBH_4$ hydrolysis yield reaching 25.4% and 25.8%, respectively, after 90 days (the experiment is still continuing). In the slurry with large amount of water ($NaBH_4$:H_2O=1:10), the rate of SB self-hydrolysis was much higher, approaching 50 mL/hr, but after 100 hrs the reaction started slowing down, and the H_2 yield reached 91.3% of theoretical. The above experiments showed that the amount of water in the slurry is critical for its long-term stability: adding excessive amounts of water greatly reduces the stability of the slurries.

4.6. Effect of Stabilizers on Long-term Stability of $NaBH_4$-H_2O Slurry

We studied the effect of stabilizers on the long-term stability of $NaBH_4$ slurries. The objective of adding stabilizers to $NaBH_4$-H_2O slurries is to suppress self-hydrolysis of $NaBH_4$ such that the dense $NaBH_4$-H_2O slurries could be safely stored onboard UUV with a minimal $NaBH_4$ degradation rate for several months (our tentative target is no greater than 1% $NaBH_4$ degradation rate over 6 months). During this reporting period, we used alkaline (NaOH) as well as a series of organic stabilizers.

Different amounts of NaOH stabilizers were added to $NaBH_4$-H_2O slurries, and $NaBH_4$ self-hydrolysis rate was determined by measuring the rate of H_2 evolution from the slurries placed

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in glass and polyethylene (PE) vials. The samples were left undisturbed for several months at room temperature. The results indicated that the long-term stability of the $NaBH_4$ slurries were substantially improved with the increase in the amount of added alkaline stabilizer. Dense (1:1) $NaBH_4$ slurries showed the degradation rates as low as 0.4% over 6 months period. More diluted slurries (1:1.2 to 1:1.5) showed the degradation rates of less than 1% over 4 months period. Slurries with relatively high water content ($NaBH_4$:H_2O ratios of 1:1.7 and 1:2) showed degradation rate higher than 1%. Fig. 10 shows typical stabilized $NaBH_4$ slurry with $NaBH_4$:H_2O ratio of 1:1.7 wt.

Fig. 10. NaOH-stabilized $NaBH_4$ Slurry.

Fig. 11 depicts the $NaBH_4$ self-hydrolysis yield in the presence of NaOH stabilizer as a function of $NaBH_4$:H_2O ratio tested over the period of about 6 months.
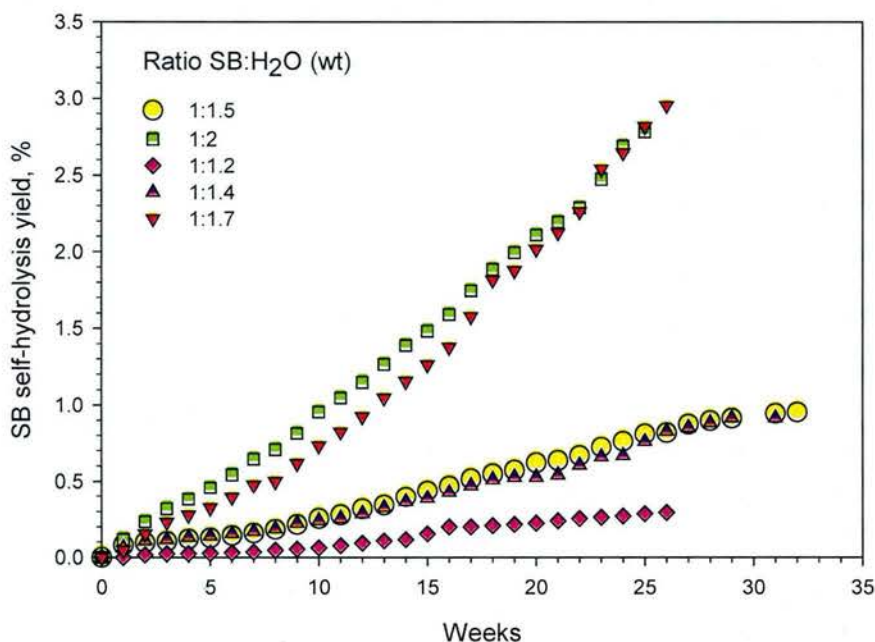

Fig. 11. Kinetics of $NaBH_4$ self-hydrolysis at different $NaBH_4$:H_2O ratios in the stabilized slurry. Amount of NaOH stabilizer in the slurry: 7.3-8.8 wt.%. Room temperature.

The experimental results indicated that the long-term stability of the NaBH$_4$ slurries is improved with the increase in the NaBH$_4$ content of the slurries (i.e., moving to higher NaBH$_4$:H$_2$O ratios). The high NaBH$_4$ content slurries (e.g., NaBH$_4$:H$_2$O ratios of 1:1, 1:1.2, 1:1.4, 1:1.5) demonstrated very good stability: below 1% NaBH$_4$ degradation rate over 6 months. However, high SB content slurries (e.g., 1:1, 1:1.2, 1:1.4) are too dense and difficult to transport from a storage container to a reactor. On the other hand, dilution of the slurries may result in the decreased stability and the overall power density of the system. In our studies, the consideration was given to these conflicting requirements, and attempts have been made to find a trade-off conditions. The results indicated that the slurries with NaBH$_4$:H$_2$O ratios in the range of 1:1.8 to 1:2 (wt) had good transportability properties, but may require some improvements in the stability.

We conducted testing of polyethylene (PE) and stainless steel (SS) materials in the presence of the alkaline stabilizer. Both materials resulted in very low NaBH$_4$ degradation rates; for example, storing stabilized NaBH$_4$-H$_2$O=1:1.5 slurry in a vial with SS foil over period of 105 days resulted in only 0.32% of NaBH$_4$ self-hydrolysis. This result implies that stainless steel (304) can be used as a potential construction material for the NaBH$_4$ slurry storage container.

Table 1 summarizes the results of long-term stability tests and hydrogen balances of NaBH$_4$-H$_2$O slurries using different stabilizers and materials.

Table 1. Hydrogen balance of stabilized SB slurries.

NaBH$_4$: carrier ratio (wt)	Slurry carrier	Amount of stabilizer in the slurry, wt.%	Duration, months	NaBH$_4$ self-hydrolysis yield (% of theor.)	Hydrogen balance, %
1:1	H$_2$O	10	9	1.2	96.8
1:1.2	H$_2$O	7.3	8	0.29	98.3
1:1.4	H$_2$O	7.7	8	0.91	97.0
1:1.5	H$_2$O	8.0	7.5	0.95	98.3
1:1.7	H$_2$O	8.1	7.5	2.9	93.2
1:2	H$_2$O	8.8	7.5	2.8	92.9
1:1.5 (PE vial)	H$_2$O	8.0	7.5	0.29	94.7
1:1.5 (SS)	H$_2$O	8.0	7.5	0.59	94.5

It was demonstrated that, in most cases, the hydrogen balance reached about 95%. Considering the experimental margin of error 5%, this evidences that no measurable NaBH$_4$ degradation through an unknown side reaction occurs in the system. The results also show that most systems meet or are close to the target of 1% NaBH$_4$ degradation rate over 6 months period.

4.7. Organic Stabilizers

We conducted a series of tests using different organic compounds as $NaBH_4$ stabilizers and carriers (since water was not present in these slurries). The organic stabilizers/carriers of interest for producing $NaBH_4$ slurries had to meet the following requirements:

- be water-soluble,
- have densities close to that of $NaBH_4$ (i.e., in the range 0.98-1.1 g/mL).
- non-volatile (boiling point much higher than that of water),
- not pyrophoric (not easily flammable, combustible),
- non-toxic,
- not chemically aggressive,
- safe-to-handle
- environmentally benign (if needed, could be discarded into the ocean and microbially digested)

We tested the following four organic stabilizers:

1) Ethylene glycol, $CH_2(OH)CH_2(OH)$, $\rho=1.109$ g/mL

2) Glycerol, $CH_2(OH)CH(OH)CH_2(OH)$, $\rho=1.26$ g/mL

3) Triethylene glycol dimethyl ether (Tri-EGDME), with density of $\rho=0.986$ g/mL

4) Tetraethylene glycol dimethyl ether (Tetra-EGDME), density $\rho=1.009$ g/mL
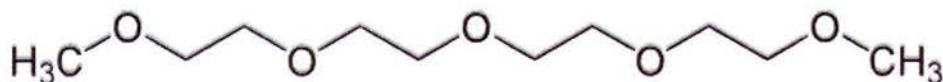
The results of testing of ethylene glycol and glycerin indicated that they were not compatible with $NaBH_4$, because they violently (exothermically) reacted with $NaBH_4$.

Both Tri-EGDME and Tetra-EGDME showed good compatibility with $NaBH_4$. Tetra-EGDME density (1.009 g/mL) is very close to that of SB (1.074 g/mL), thus, it forms a relatively stable slurry with $NaBH_4$. $NaBH_4$ slurries in Tetra-EGDME with $NaBH_4$: Tetra-EGDME ratios of 1:1.5 to 1:2 also demonstrated good flowability (see Fig. 12). In contrast, Tri-EGDME has much lower density than $NaBH_4$, so it quickly precipitates, and, as such, is not good for preparing stable $NaBH_4$ slurries.
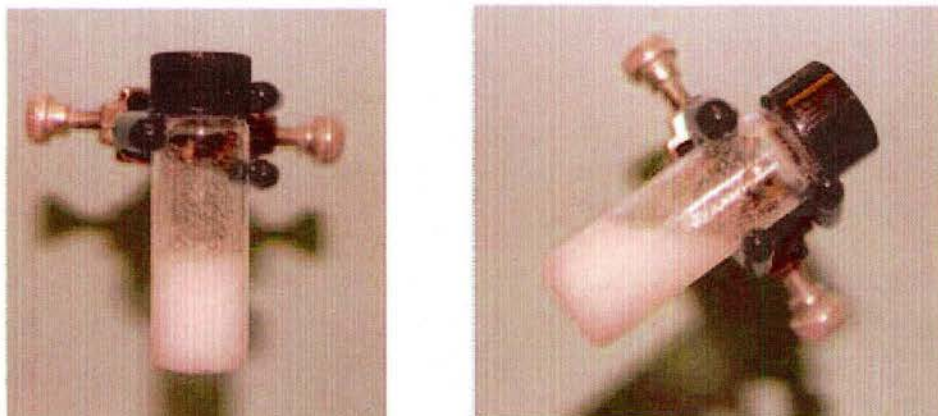
Fig. 12. NaBH₄ slurry in Tetra-EGDME. Ratio NaBH₄: Tetra-EGDME=1:1.6 wt.

$NaBH_4$ was mixed with stabilizers/carriers in 1:1, 1:1.5 and 1:2 ratios (wt) in glass vials, and the vials were connected to H_2 measuring device to determine the $NaBH_4$ degradation rate and long-term stability of the slurries. The results are presented in Table 2.

Table 2. NaBH₄ degradation rates in presence of organic carriers/stabilizers.

Carrier-stabilizer	NaBH₄-carrier ratio in slurry (wt)	Duration days	Amount of H_2, mL	Extent of NaBH₄ hydrolysis (% of theor.)	Comment
Ethylene glycol	1:1	-	-	-	Violently reacts with SB
Glycerin	1:1	-	-	-	Violently reacts with SB
Tri-EGDME	1:1	90	30.0	2.4	Compatible with SB
Tetra- EGDME	1:1	45	19.2	1.5	Compatible with SB
Tetra- EGDME	1:2	90	4.2	0.3	Compatible with SB
Tetra- EGDME in PE vial	1:1.5	80	12.3	0.98	Tetra-EGDME is compatible with PE
Tetra- EGDME in vial with SS foil	1:1.5	80	4.8	0.38	Compatible with SS

Tri-EGDME - triethyleneglycol dimethyl ether; Tetra-EGDME - tetraethyleneglycol dimethyl ether. SB- sodium borohydride.

The tests showed that $NaBH_4$ degradation rate in Tri-EGDME was higher than that in Tetra-EGDME (during the same time period). The degradation rate of $NaBH_4$ in $NaBH_4$: Tetra-EGDME slurry with the ratio of 1:2 wt. was only 0.3% over 90 days. More dense slurry (e.g., 1:1) showed slightly higher degradation rate.

Table 3 shows the results of testing of Tetra-EGDME stabilizer over period of up to 7 months. One experiment involved combination of NaOH and Tetra-EGDME stabilizers. The hydrogen balance measurements are also included in the Table 3.

Table 3. The results of testing of Tetra-EGDME stabilizer over 6.5-7 months and hydrogen balance of the system.

$NaBH_4$: carrier ratio (wt.)	Slurry carrier	Amount of NaOH stabilizer in the slurry, wt.%	Duration, months	$NaBH_4$ self-hydrolysis yield (% of theor.)	Hydrogen balance, %
1:1.5 (SS foil)	Tetra-EGDME	None	6.5	1.4	94.3
1:2	Tetra-EGDME	None	7	2.1	93.8
1:1.5 (PE vial)	Tetra-EGDME	None	6.5	3.4	92.2
1:2*	H_2O: Tetra-EGDME (1:1 wt)	8.8	2.5	3.0	93.0

*non-stable slurry

We checked for the possibility that Tetra-EGDME might have reacted with SB without releasing hydrogen by conducting the following experiment. $NaBH_4$:Tetra-EGDME=1:1 (wt) slurry was kept for 12 days at room temperature, and then was transferred into a flask where diluted sulfuric acid (0.1M) was added drop-wise until $NaBH_4$ acid hydrolysis was completed. The volume of released hydrogen was accurately measured and hydrogen balance determined. The total amount of H_2 evolved corresponded to 95.2% of theoretical amount of hydrogen in $NaBH_4$. Considering the margin of error of the experiment 5%, this experiment showed that practically no chemical interaction between $NaBH_4$ and Tetra-EGDME occurred during 12 days of storage.

We also conducted long-term testing of $NaBH_4$- Tetra-EGDME (1:1.5) slurries in polyethylene (PE) vial and in a glass vial containing stainless steel (SS) foil. The $NaBH_4$ degradation rates with PE and SS were found to be 3.4% and 1.4%, respectively, over period of 6.5 months.

In general, the NaBH$_4$ slurries based on tetraethyleneglycol dimethyl ether (Tetra-EGDME) showed good long-term stability: NaBH$_4$ self-hydrolysis yield of 2.1% over period of 7 months (note that no water was present in the slurries). Combination of tetra-EGDME with NaOH (50:50), as well as the addition of small amount of tetra-EGDME to NaOH based slurries did not improve the stability of the slurries. The slurry with triethyleneglycol dimethyl ether (Tri-EGDME), although, being compatible with NaBH$_4$, did not show good long-term stability.

The NaBH$_4$ acid hydrolysis experiments showed excessive foam formation during NaBH$_4$ hydrolysis in the presence of tetra-EGDME, which would complicate production of H$_2$ onboard UUV. The possible effect of tetra-EGDME vapor on the stable function of PEMFC is another unknown. Based on the above considerations, tetra-EGDME and tri-EGDME stabilizers will not be pursued in future work.

4.8. Effect of Materials on the Stability of NaBH$_4$ Slurries.

Tests on the effect of stainless steel (SS) and polyethylene (PE), polycarbonate, carbon steel, brass and copper materials on the long-term stability of NaBH$_4$ slurries in the presence of alkaline stabilizer were conducted. The results of the tests conducted over about 8 months are shown in Table 4.

Table 4. The effect of different materials on NaBH$_4$ self-hydrolysis over 8 months period

Materials	Compatibility with NaBH$_4$	Comment
Glass	🟢	Inert
Polyethylene	🟢	Inert
Polycarbonate	🔴	Reacts
Carbon steel	🔴	Catalyzes
Stainless steel (304)	🟢	Inert
Stainless steel *	🟡	Slight. cat.
Copper	🔴	Catalyzes
Brass	🔴	Catalyzes

🟢 Compatible
🟡 Moderately compatible
🔴 Incompatible

* Stainless steel for medical applications

It was found that the NaBH₄ self-hydrolysis yield in stabilized NaBH₄:H₂O=1:1.5 wt. slurry that was in contact with stainless steel and PE over period of 8 months were below 1% (of the theoretical amount of H₂). PE proved to be the most inert material with regard to degradation of NaBH₄ slurries. This demonstrates that both SS-304 and PE can be used as construction materials for NaBH₄ storage vessels.

4.9. Effect of Ultrasonication on the Formation and Stability of NaBH₄ Slurries.

The new method for formation and stabilization of NaBH₄ slurries was developed. The method is based on ultrasonication (frequency of >20 kHz) of the SB slurries for the short period of time (5-15 min). Control experiments showed that no NaBH₄ self-hydrolysis was initiated or accelerated during the ultrasonication procedure. The results also indicate that the ultrasonication process did not adversely impact the long-term stability of the slurries. This preparation method allowed producing uniform slurries with lesser amount of the alkaline stabilizer (by about factor at least two). The results are shown in Fig. 13.
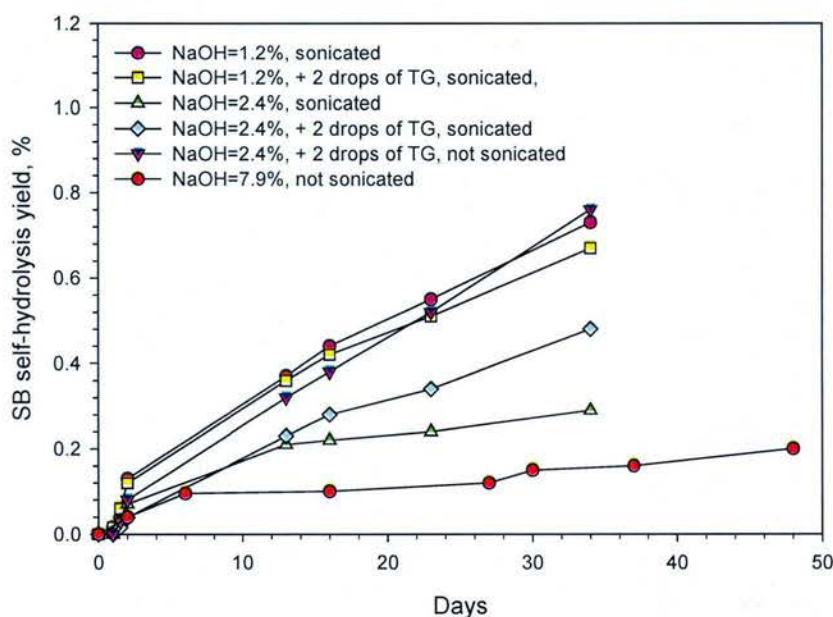

Fig. 13. Kinetics of NaBH₄ self-hydrolysis in NaBH₄:H₂O=1:1.5 slurry produced by ultrasonication for 15 min. Amount of NaOH stabilizer is variable. TG is tetra- EGDME.

The experiemnts showed that the NaBH₄ slurries could be stabilized with the amount of the stabilizer in the slurry as low as 1.2%. Adding a small amount of tetra-EGDME to the slurry did not improve its stability. Fig. 14 shows stabilized NaBH₄ slurry after ultrasonication.
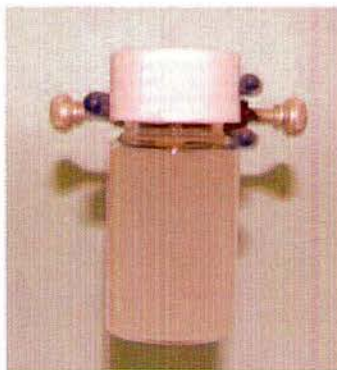
Fig. 14. Stabilized NaBH₄ slurry after exposure to ultrasonication for 10 min

4.10. Testing of Transportability of NaBH₄ Slurries.

The feasibility of delivering NaBH₄ slurries to the hydrolysis reactor using a syringe pump was demonstrated. The NaBH₄ slurries with the ratio of NaBH₄:H₂O=1:1.8 and 1:2 were loaded to a plastic (polyethylene) syringe, and were delivered through a Teflon (PTFE) tubing (1/8 inch) to a hydrolysis reactor. The stabilized slurry NaBH₄:H₂O=1:2 performed best. The NaBH₄ slurry was delivered to the hydrolysis reactor where it reacted with Al particles at 80°C to produce the stream of pure H₂. The amount of H₂ produced with relatively high accuracy (94.7%) corresponded to the stoichiometry of hydrolysis of NaBH₄ and Al reagents. This experiment demonstrated that NaBH₄ slurries can be safely stored and on-demand transported to a hydrogen generation reactor.

4.11. Development of Al Slurries.

Attempts have been made to develop Al powder slurries, which turned out to be not an easy task. Al powder with the average size of 20 u was used in these experiments. Al has relatively high density (ρ=2.70 g/mL), thus, finding suitable carrier for the Al slurry presents a bigger challenge than for SB. We have tested Tetra-EGDME as a carrier for the Al slurry. The tests showed that Al and Tetra-EGDME are compatible and do not react at ambient conditions. Al powder was added to Tetra-EGDME in 1:1.7 ratio, and its degradation rate was measured over period of 70 days. No hydrogen evolution or any other visible chemical change was observed during the testing period. The results indicated that Al can be stored in Tetra-EGDME for extended period of time without degradation. However, the mechanical stability of the slurry was not adequate: Al powder easily separated from the carrier within minutes, implying that Tetra-EGDME is not a suitable carrier for the Al slurry. In another series of experiments we tested water-soluble viscous polymer. Al powder readily formed slurries with water-soluble viscous polymeric compound that were stable for a day or two, but gradually Al powder precipitated over 10-15 days period The work on development of Al slurries is still in progress.

4.12. NaBH₄ Storage in the Form of Dense and Super-saturated Aqueous Solutions

$NaBH_4$ dense solutions (DS) exist at the borderline of physical solubility of SB in water at given temperature, typically, corresponding to the dilution factor of $NaBH_4$:H_2O close to 1:2 (wt), (note that $NaBH_4$ solutions used in traditional metal-catalyzed hydrolysis systems feature dilution factors of 1:5 to 1:10). $NaBH_4$ super-saturated solutions (SSS) are relatively stable aqueous systems representing dense solutions that may contain suspended micro-particles. SSS represent a middle ground between slurries and DS.

Table 5 summarizes the data on the degradation rates of $NaBH_4$ dense solutions and SSS during 3 to 4 months storage experiments using different stabilizers, concentrations of stabilizers, ultrasonication pretreatment and materials. The data on the extent of H_2 recovery from the $NaBH_4$ storage systems are also included in the Table 5, as a percentage of the stoichiometrically (i.e., theoretically) recoverable amount of hydrogen contained in $NaBH_4$. The hydrogen balance of the studied $NaBH_4$ storage systems is also included, which takes into consideration the amount of H_2 released during self-hydrolysis over storage period and the amount of H_2 formed during forced acid-hydrolysis of the slurries at the end of the test.

Table 5. Summary of Testing of $NaBH_4$ Dense Solutions and SSS for Long-term Energy Storage

No:	NaBH₄ : H₂O (wt)	Conc. of sta-bilizer (M)	Ultra-soni-cation	Slurry or dense solution (SL or DS)	Duration (months)	NaBH₄ self-hydrolysis yield (%)	Amount of H₂ recovered (% of theor.)	H₂ balance (%)
1	1:1.8	1.5	No	DS	4	1.47	94.8	96.3
2	1:1.8	2.5	Yes	DS	4	1.03	98.3	99.3
3	1:1.8	2.5	No	SSS	3.5	0.94	97.3	98.2
4	1:1.8	5	No	SSS	3.5	0.23	95.1	95.3
5	1:1.8	5	Yes	SSS	3.5	0.15	99.4	99.5
6	1:2	3.3	Yes	DS	4	0.73	98.4	99.1
7	1:2	2.5	No	DS	3.5	1.21	94.3	95.5
8	1:2	5	Yes	DS	4	0.21	101.5	101.7
9	1:2	5	No	SSS	3.5	0.21	99.9	100.2
10	1:2	5	Yes	DS	3.5	0.3	100.8	101.1

As can be seen from the Table 5 that, in most cases, the hydrogen balance exceeds 95%. Considering the experimental margin of error 5%, this evidences that practically all hydrogen in the system is accounted for and no appreciable $NaBH_4$ degradation through an unknown side reaction occurs in the system. It was found that the transition zone between $NaBH_4$ dense solutions and SSS corresponded to the $NaBH_4$: H_2O dilution factor varying from 1:1.8 to 1:2 (wt), depending on the concentration of the NaOH stabilizer. Higher stabilizer concentrations tend to shift the transition point to lower dilution factors. It was found that in a wide range of stabilizer concentrations, the dilution factor 1:2 is adequate to produce stable uniform dense solutions that can be easily transported via a variety of pumping options. Ultra-sonication of the dense solutions improves their uniformity and stability.

Table 6 summarizes the data on the degradation rates of $NaBH_4$ slurries and dense solutions using alternative stabilizers during 3.5-4 months experiments. Different $NaBH_4$:H_2O ratios, stabilizers, concentrations of stabilizers, ultrasonication pretreatment, as well as effect of materials have been tested in these experiments. Several new approaches to enhancing chemical and mechanical stability of slurries have been tested during this reporting period, in particular, using KOH as a stabilizer, and combining $NaBH_4$ with potassium borohydride (KBH_4). KBH_4 has slightly better chemical stability in aqueous solutions (i.e., it is less reactive with water) than $NaBH_4$, and it has slightly higher density. In the series of experiments testing new stabilizing systems, KOH was used instead of NaOH, and $NaBH_4$ was mixed with KBH_4 in the ratios 4:1 and 3:2, by weight.

Table 6. Long-term Stability of $NaBH_4$ Dense Solutions and SSS

No	$NaBH_4$: H_2O (wt)	Stabilizer	Conc. of sta-bilizer (M)	Ultra-soni-cation	Dense solution or SSS	Duration (months)	$NaBH_4$ hydrolysis yield (%)	Amount of H_2 recovered (%)	H_2 balance (%)
1	1:1.8	KOH	2.5	Yes	SL	4	1.17	95.9	97.3
2	1:2	KOH	2.5	Yes	SL	4	1.27	95.7	97.0
3	1:1.5 (SB:PB= 4:1 wt.)	NaOH/KBH$_4$	5	Yes	SL	3.5	0.35	98.9	99.3
4	1:1.5 (SB:PB= 4:1 wt.)	NaOH/KBH$_4$	5	Yes	SL	3.5	0.25	97.6	97.8
5	1:1.5 (SB:PB= 3:2 wt.)	NaOH/KBH$_4$	5	Yes	SL	3.5	0.49	101.2	101.7
6	1:2 (PE)	NaOH	5	No	DS	3.5	0.05	97.6	97.7
7	1:2 (SS foil)	NaOH	5	No	DS	3.5	0.06	99.8	99.9
8	1:1.8 (SS*)	NaOH	2.5	No	DS	3.5	1.41	96.5	97.9

SB - sodium borohydride, PB- potassium borohydride, SL – slurries, DS- dense solutions, PE- polyethylene, SS- stainless steel 304, SS*- stainless steel for medical applications.

As can be seen from the Table 6, in most cases, the hydrogen balance exceeds 95%, which evidences that practically all hydrogen in the system is accounted for and no appreciable SB degradation through an unknown side reaction occurs in the system.

Table 7 summarizes the effect of different stabilizers on the chemical and mechanical stability of $NaBH_4$.

Table 7. Effect of Different Stabilizers on Chemical and Mechanical Stability of $NaBH_4$.

$NaBH_4$ Stabilizers	Chemical stability	Mechanical stability
H_2O (no stabilizer)	🔴	🔴
NaOH (0.1-5.0M)	🟢	🟢
KOH (2.5M)	🟡	🟢
KBH_4	🟢	🟢
Organic ethers (Tri-EGDME, Tetra-EGDME)	🔴	🟡
Gelling polymers	Still testing	🟢
Sonication (20 kHz)	🟢	🟢

Green ovals- good, Yellow – intermediate, Red- poor.

The experiments indicated that replacing NaOH stabilizer with KOH based stabilizer did not improve the stability of the $NaBH_4$ slurries. On the other hand, the combination of two hydrides ($NaBH_4$ and KBH_4) in the presence of NaOH stabilizer resulted in the improvement in mechanical and chemical stability of the slurries. Most likely, this is due to slightly greater density of KBH_4 compared to $NaBH_4$ which enables better match in the density of solid and liquid phases in the $NaBH_4$ slurry. Furthermore, KBH_4 is less reactive than $NaBH_4$ in aqueous solutions which also adds to the improved chemical stability. However, the increase in the system stability due to the presence of KBH_4 is not dramatic, so it does not justify further complication of the system by including an additional component.

Fig. 15 summarizes data on the chemical stability of some $NaBH_4$ storage systems.
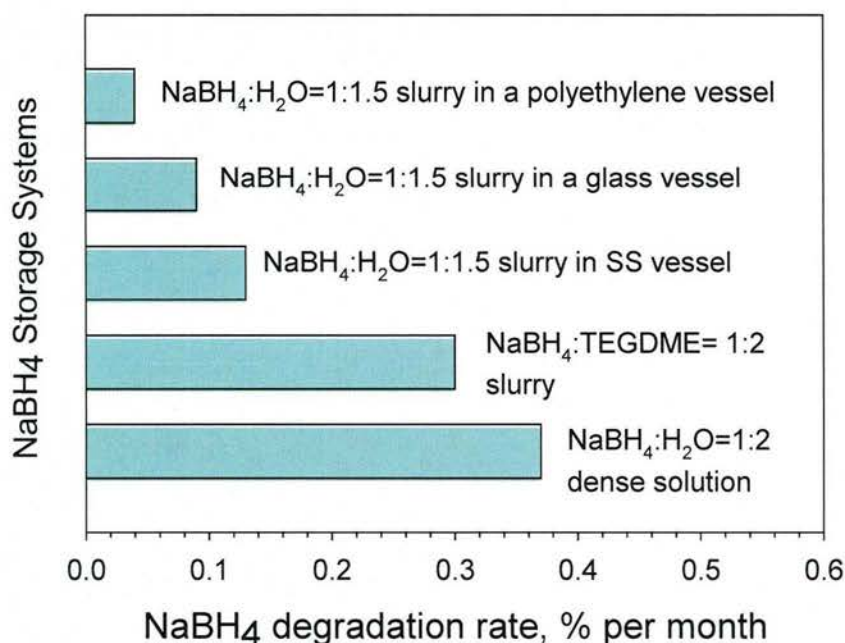
Fig. 15. NaBH$_4$ degradation rate in stabilized slurries and
dense solutions during 6 months long tests

As can be seen from the Fig. 15, storing NaBH$_4$ slurries or dense solutions in polyethylene vessels shows the least degradation rate.

4.13. Effect of Seawater on Kinetics of NaBH$_4$ and Al-NaBH$_4$ Hydrolysis

We conducted a series of experiments on the effect of seawater on the kinetics NaBH$_4$ and Al- NaBH$_4$ hydrolysis with production of H$_2$. The rational was to determine whether seawater can be used for on-board production of hydrogen instead of using DI water that have to be carried on-board. Seawater was collected from the Atlantic Ocean near the city of Melbourne, FL. Seawater was twice filtered to remove particulate matter.

4.13.1 Effect of Seawater Minerals

We studied the effect of seawater and individual seawater minerals on the kinetics of NaBH$_4$ hydrolysis alone (i.e., without Al present). The major seawater minerals and their average molar (M) concentrations are as follows:

NaCl ~ 0.5; MgCl$_2$ ~ 0.05; Na$_2$SO$_4$ ~ 0.03.

The solutions of NaCl, MgCl$_2$ and Na$_2$SO$_4$ in DI water close to the above concentrations range were prepared and tested. NaOH-stabilized SB dense solutions (SB:H$_2$O=1:2 w.) were added to seawater and to the solutions of individual seawater minerals. The reacting solutions were mixed with a magnetic stirrer and placed in a bath maintained at 60°C; the amount of H$_2$ released was measured with the accuracy of ±2%. The results are presented in Fig. 16. For the comparison, the kinetic curve of H$_2$ evolution from DI water at the same conditions is also included in the diagram.
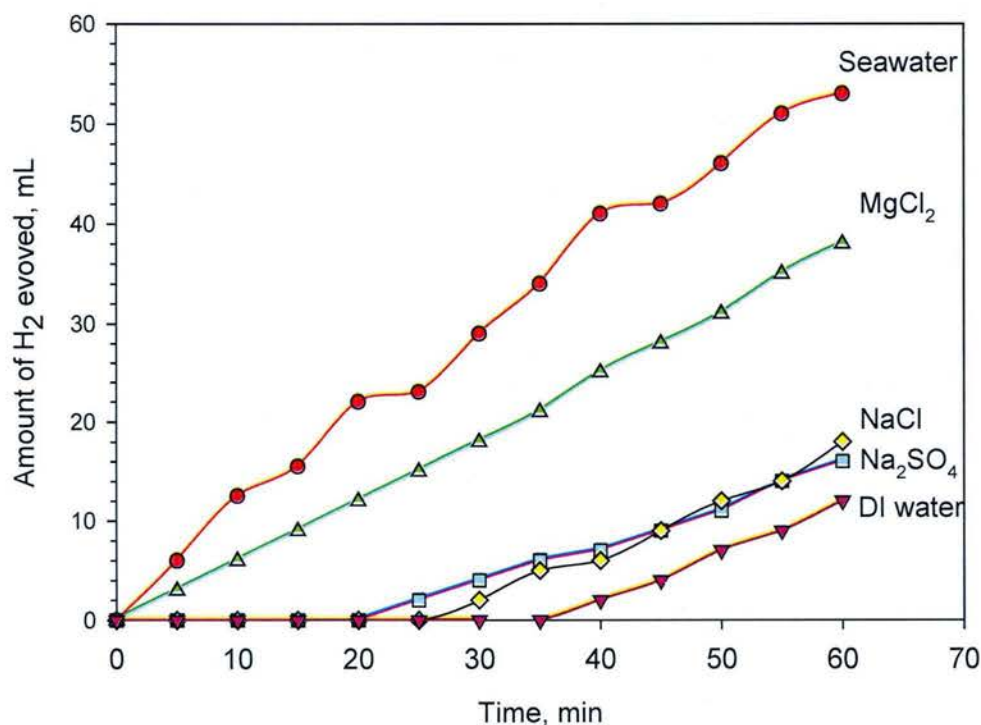

Fig. 16. Effect of seawater and its minerals on the kinetics of H$_2$ evolution. NaBH$_4$ dense solution with ratio of NaBH$_4$:H$_2$O=1:2 w. [NaCl]=0.5M, [MgCl$_2$]= 0.1M, [Na$_2$SO$_4$]=0.05M. T= 60°C.

It is evident from the diagram that seawater has a significant accelerating effect on NaBH$_4$ hydrolysis. Among seawater minerals, NaCl and Na$_2$SO$_4$ have a negligible effect on the kinetics of NaBH$_4$ hydrolysis, whereas, MgCl$_2$ showed a significant impact on the reaction. Thus, the presence of Mg salts is largely responsible for the accelerating effect of seawater on NaBH$_4$ hydrolysis.

4.13.2. Effect of Seawater on the Al-NaBH$_4$ Hydrolysis

Fig. 17 A and B show the kinetic curves of H$_2$ production by Al- NaBH$_4$ hydrolysis in DI water and seawater at 80°C (A) and 95°C (B). Al powder was put in a flask placed in a thermostat bath. NaOH-stabilized NaBH$_4$ dense solution (NaBH$_4$:H$_2$O=1:2 w.) was injected to the flask and the amount of H$_2$ evolved was accurately measured.
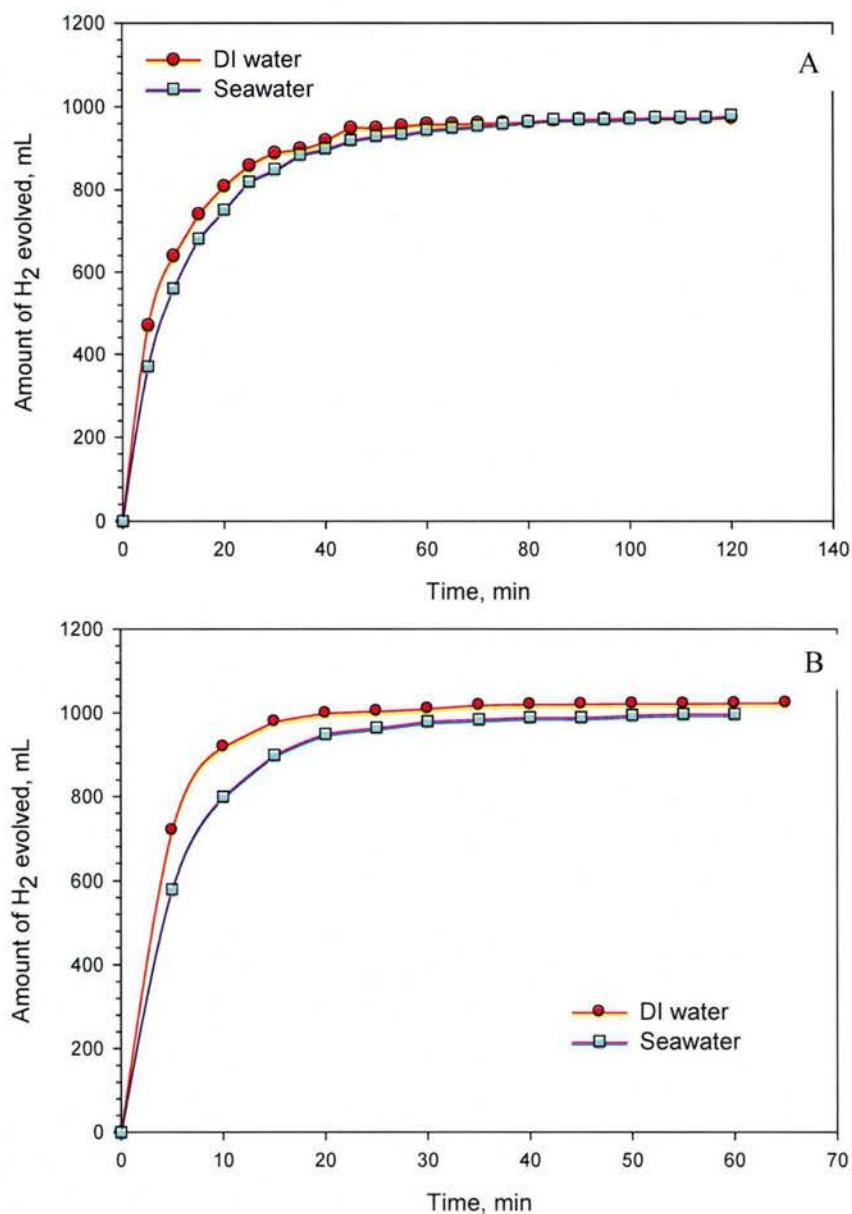
30

Fig. 17. Kinetics of Al- NaBH$_4$ hydrolysis in DI water and seawater at 80°C (A) and 95°C (B). NaBH$_4$ dense solution with ratio of NaBH$_4$:H$_2$O=1:2 w. was used in the experiments.

The experiments demonstrated that seawater does not significantly affect the kinetics of Al-SB hydrolysis. Within the margin of experimental error, the amount of H$_2$ produced from the reacting system is almost the same in both DI and seawater and is equal to stoichiometric amount of H$_2$.

4.13.3. Effect of Seawater on the Synergistic Hydrolysis of Al-SB System

In the following series of experiments, the effect of seawater on synergistic action during combined Al- $NaBH_4$ hydrolysis was elucidated. Each series consisted of three experiments carried out in DI water and seawater: hydrolysis of Al powder alone, hydrolysis of $NaBH_4$ solution alone, and hydrolysis of Al- $NaBH_4$ mixture. The experiments were conducted at 60°C. The results are depicted in Fig. 18 (A and B).
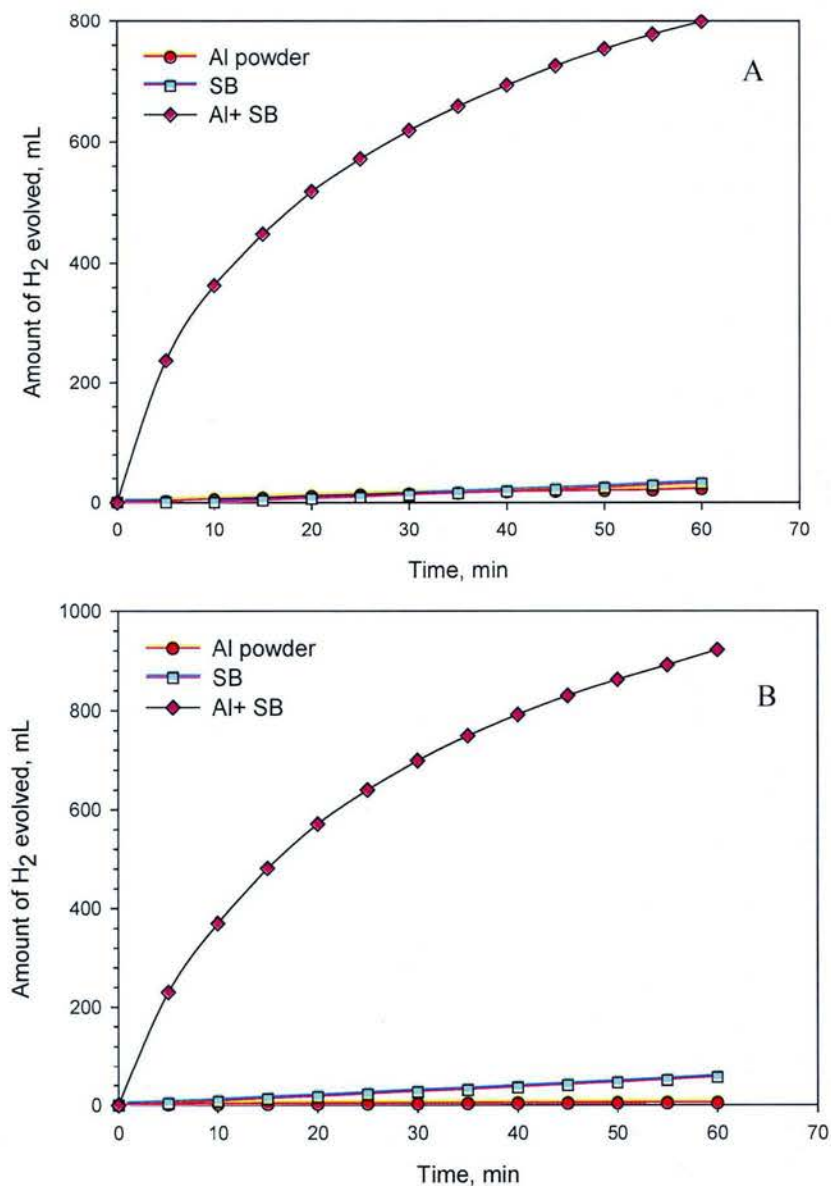

Fig. 18. Effect of seawater on synergistic action of Al- $NaBH_4$ hydrolysis. Al powder (size: 20 micron, 0.5g). $NaBH_4$:H_2O dense solution (1:2 w). Temperature 60°C. A-experiments conducted in DI water, B- experiments conducted in seawater

The experiments showed that seawater had no inhibiting effect on the kinetics of H_2 production from Al- $NaBH_4$ mixture and on the synergistic action of combined Al- $NaBH_4$ hydrolysis.

4.14. Effect of Products of Al Hydrolysis on $NaBH_4$ Hydrolysis.

The objective of the experiments described in this section is to elucidate the role of products of Al hydrolysis as catalytic agents for $NaBH_4$ hydrolysis. As shown in our previous work, the presence of Al powder has a significant catalytic effect on $NaBH_4$ hydrolysis, but is the role of products of Al hydrolysis? To answer this question we used the products of Al hydrolysis: Al oxide: Al_2O_3 (in the form of nano-powder) and Al hydroxide: $Al(OH)_3$. If products of Al hydrolysis have catalytic activity in $NaBH_4$ hydrolysis, their role in catalyzing the overall process may become substantial as the reaction progresses and the amount of the reaction products increases. Al hydroxide in the form of gel used in the experiments was collected after conducting Al hydrolysis in DI water at elevated temperature. The effect of Al hydrolysis products on $NaBH_4$ hydrolysis rate are presented in Fig. 19. For the comparison, the kinetic curve of $NaBH_4$ hydrolysis in DI water at the same temperature (80°C) is also included in the diagram. The experiments indicated that Al oxide did not exert any catalytic effect on $NaBH_4$ hydrolysis. Although, Al hydroxide shows some catalytic activity in $NaBH_4$ hydrolysis reaction, the amount of H_2 produced is rather low, and it cannot explain the significant increase in $NaBH_4$ hydrolysis rate in the presence of Al powder. Thus, most of catalytic effect of Al powder on $NaBH_4$ hydrolysis can be attributed to metallic Al.
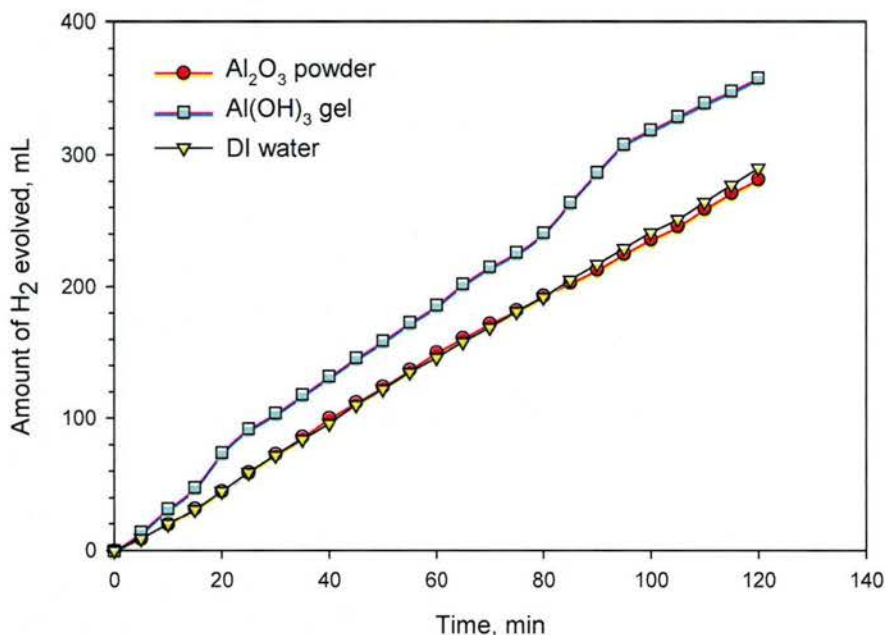

Fig. 19. Effect of Alumina (Al_2O_3) powder and Al hydroxide gel on the kinetics of H_2 release from $NaBH_4$ solutions in DI water. Amount of Al oxide and hydroxide: 0.3 g. T= 80°C.

4.15. Production of Hydrogen by Al-NaBH$_4$ Hydrolysis in a Batch Reactor

We conducted a series of experiments on combined Al-NaBH$_4$ hydrolysis, as well as separate hydrolysis of NaBH$_4$ and Al at 80°C in a batch reactor. The results are presented in Fig. 20, which clearly demonstrates the synergistic action of Al and NaBH$_4$ reagents in the hydrolysis reaction.
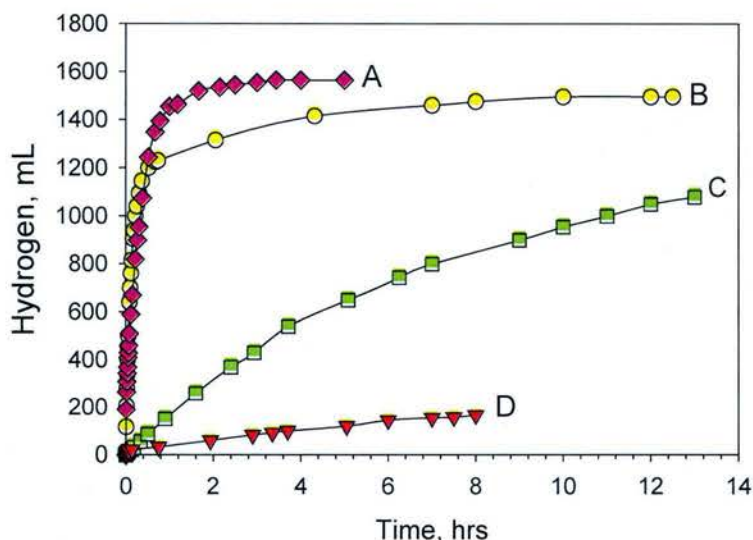

Fig. 20. Kinetic curves of combined and separate Al and NaBH$_4$ hydrolysis.
Al 0.25g, NaBH$_4$ 0.50g. Al:NaBH$_4$=1:2 wt. Stabilizer: 0.5M NaOH. Temperature 80°C.
Deionized water 10 mL.
A- Al, NaBH$_4$ and NaOH stabilizer are present,
B- Al and NaBH$_4$ are present (no stabilizer).
C- Stabilized NaBH$_4$ solution (no Al),
D- Al powder in deionized water.

It can be seen that the presence of NaOH stabilizer in the Al-NaBH$_4$ system allowed achieving complete hydrolysis in shorter time period compared to the system without the stabilizer. Thus, the advantages of adding NaOH stabilizer are two-fold: it improves NaBH$_4$ long-term storage stability and it also facilitates the Al-NaBH$_4$ hydrolysis kinetics to achieve complete conversion of reagents.

4.16. Continuous Production of Hydrogen by Al-NaBH$_4$ Hydrolysis in a Glass Reactor

We've assembled an experimental unit for the continuous production of pure hydrogen stream by combined hydrolysis of Al and NaBH$_4$. Al powder was placed in the hydrolysis reactor, and NaBH$_4$ in the form of stabilized dense solution (shown in upper right corner) with NaBH$_4$:H$_2$O ratio of 1:2 (wt) was delivered to the reactor by a plastic syringe pump through an 1/8 inch Teflon tubing. The reaction temperature was measured by a

thermocouple placed inside the hydrolysis reactor. The hydrogen flow was measured and recorded every 10 s by a mass flow meter connected to LabView data acquisition system.

Fig. 21. depicts the photo of the experimental setup used for the continuous production of hydrogen by Al-NaBH₄ hydrolysis in deionized water.
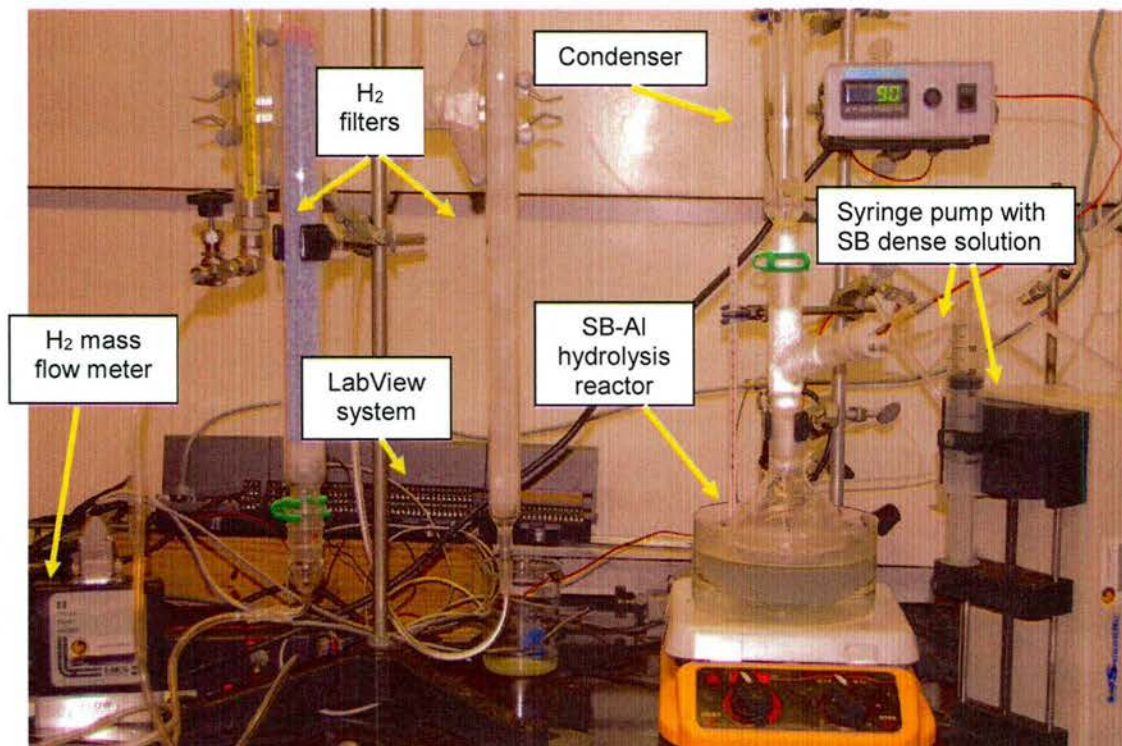

Fig. 21. Experimental setup used for the continuous production of hydrogen by Al-NaBH₄ hydrolysis in deionized water using a glass reactor. Hydrolysis temperature: 90±2°C.

Fig. 22 shows stabilized NaBH₄ dense solution (NaBH₄:H₂O=1:2 wt) which was loaded in the 60 mL plastic syringe and was delivered by a syringe pump to the hydrolysis reactor containing Al powder.

Fig. 22. NaOH-stabilized NaBH$_4$ dense solution (NaBH$_4$:H$_2$O=1:2 wt) used for continuous production of hydrogen by Al-NaBH$_4$ hydrolysis.

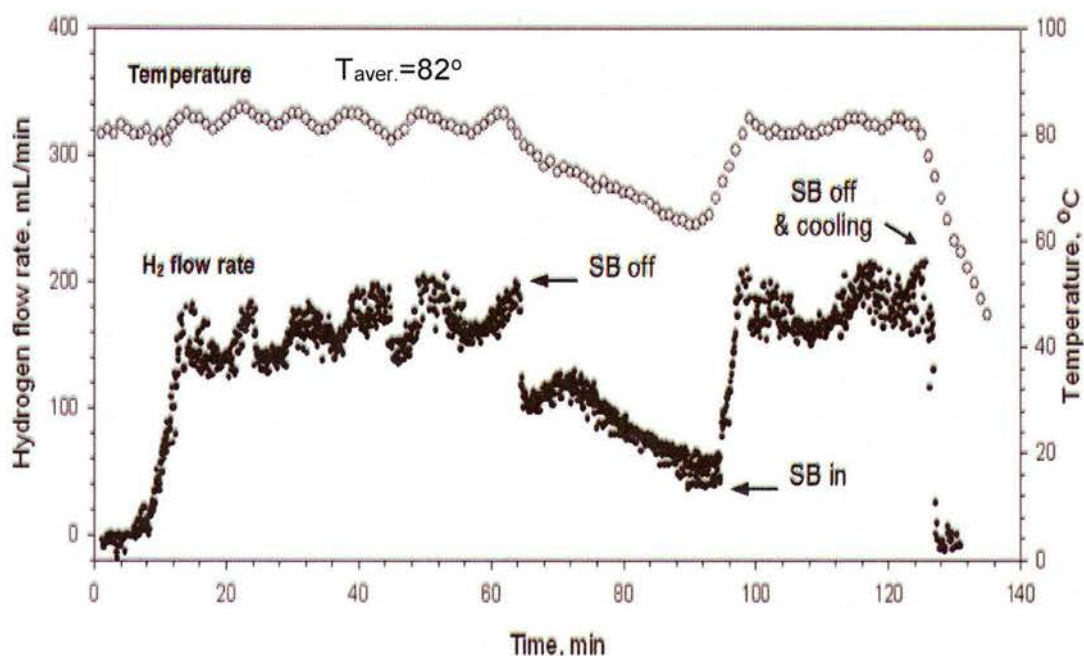Fig. 23 shows the LabView-recorded hydrogen flow data along with temperature data.

Fig. 23. Continuous production of hydrogen by Al-NaBH$_4$ hydrolysis at 82°C using a glass reactor.

During the Al-NaBH$_4$ hydrolysis experiment, average temperature of 82°C was maintained in the reactor. Due to exothermic nature of the Al-NaBH$_4$ hydrolysis reaction, temperature in

the reactor varied by about $\pm 3°C$ during the experiment. This resulted in a wavy shape of the hydrogen production curve, which was in synch with the temperature curve. After 65 min, the delivery of $NaBH_4$ dense solution to the reactor was cut-off, with temperature remaining at the same level. This resulted in reduced H_2 production rate, which was mostly due to hydrolysis of unreacted Al powder. After resuming $NaBH_4$ delivery, H_2 production rate returned to about the same level as it was before the $NaBH_4$ interruption. At the end of experiment (after 125 min), $NaBH_4$ delivery was cut-off and temperature was reduced to about 50°C, which resulted in almost immediate cessation in H_2 production. The experiment demonstrated that H_2 flow from the reactor can be regulated by varying two parameters: the rate of $NaBH_4$ delivery and temperature. Hydrogen produced in the hydrolysis reactor was filtered through a column with quartz wool to remove mist and through a column with a drierite bed to remove excessive moisture before it was measured by a mass flow meter. In the integrated system involving PEMFC, the removal of moisture will not be necessary.

Fig. 24 shows the results of the hydrogen production experiment at somewhat higher temperature (90°C) as recorded by the LabView data acquisition system. At the beginning of the experiment, and during the experiment there were short periods of thermal instability due to the exothermic nature of the hydrolysis reaction; but in every case, the thermal regime and H_2 production rate were stabilized through a temperature control.
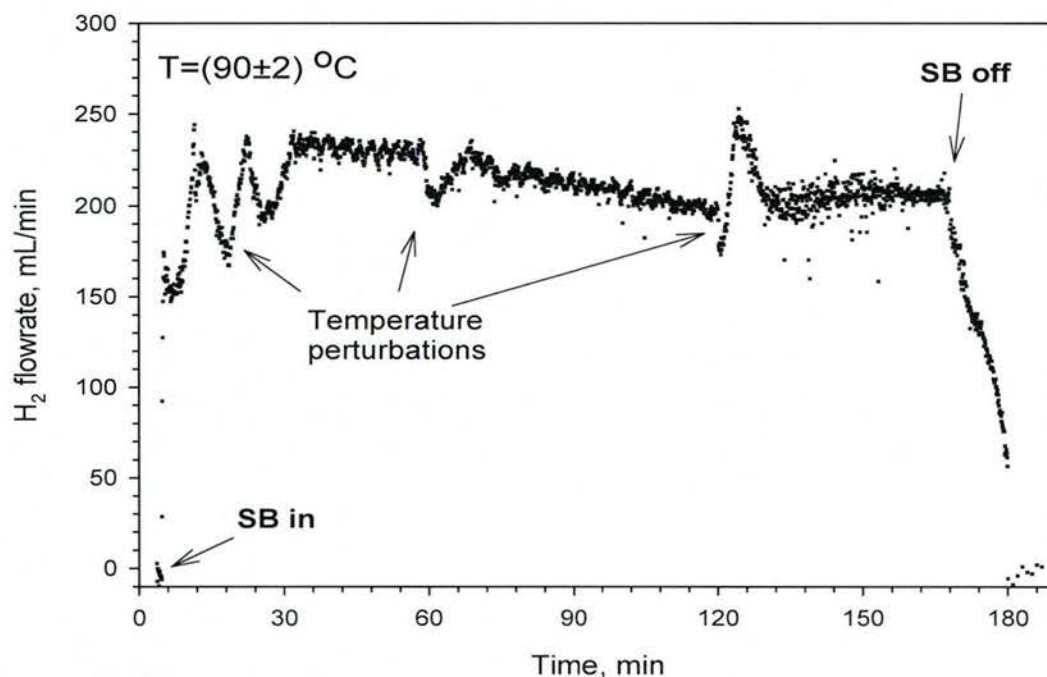

Fig. 24. Continuous production of hydrogen by Al-$NaBH_4$ hydrolysis at 90±2°C.

The comparison of the experiments shown in Figs. 23 and 24 indicates that, in general, the temperature regime and H_2 production rates are more stable at the higher level of temperature. As in the previously-described experiment, cutting off SB delivery and cooling the reactor results in the stopping of H_2 production.

4.17. Continuous Production of Hydrogen by Hydrolysis of Al-NaBH₄ in Stainless Steel Reactor.

A stainless steel (304) reactor (diameter of 5 cm and height of 14 cm) was designed and fabricated for conducting hydrolysis of Al-NaBH₄. The reactor had 2 inlets and one outlet. The reactor was equipped with a filter to remove the mist that could be carried out by hydrogen from the reactor. The tubular filter was filled with glass wool. Temperature and pressure inside the reactor can be controlled with adequate accuracy.

Fig. 25 depicts the experimental setup including the hydrolysis reactor and the NaBH₄ reagent delivery system using a syringe pump. Operational conditions of the reactor could be varied in the following range: temperature up to 95°C, pressure 1 (but could be increased to 10 atm). Temperature control system allows to maintain the temperature within ±1°C deviation. Note that during operation, the reactor was wrapped with a fiberglass insulator (not shown in Fig. 25).

Fig. 25. Experimental setup with a stainless steel hydrolysis reactor for continuous production of hydrogen stream.

Fig. 26 shows the results of the hydrogen production experiment using stainless steel hydrolyzer as recorded by the LabView data acquisition system.
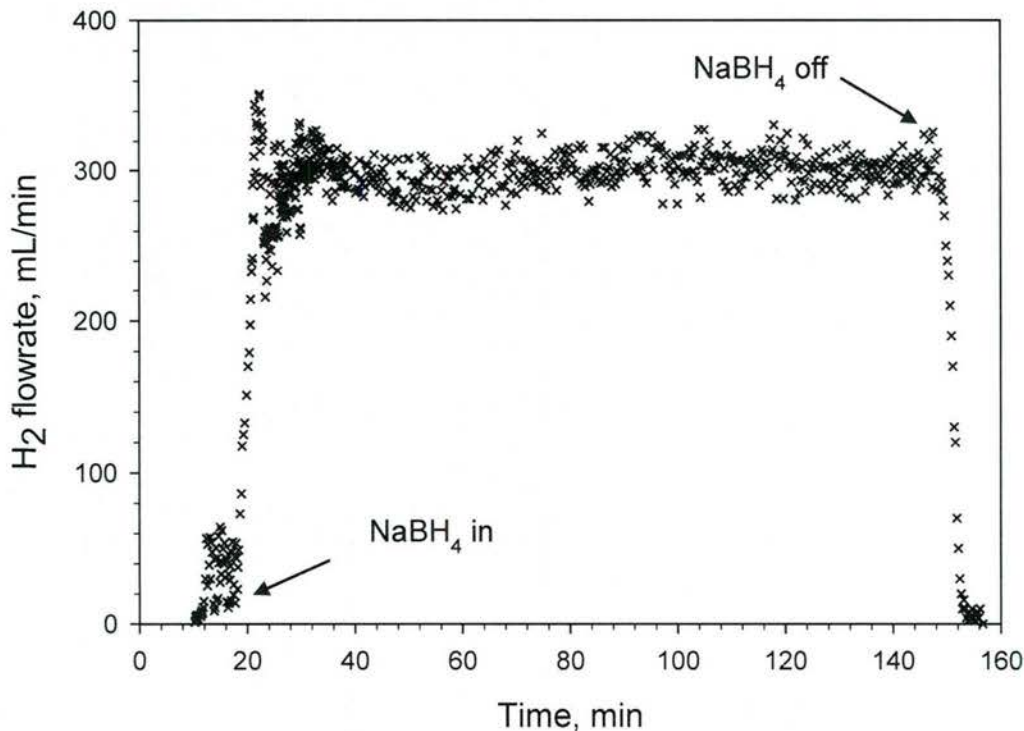
Fig. 26. Continuous production of hydrogen by Al-NaBH₄ hydrolysis in stainless steel reactor. Temperature 92±1°C. Al powder (20 micron). NaBH₄ dense solution (1:2 wt).

Due to better temperature control, we observed fairly steady-state production of stream of high-purity hydrogen (although, initially, there was some insignificant and short-term instability in the system). This experiment demonstrated that the optimal temperature regime for the Al-NaBH₄ hydrolysis reaction is in the range of 90-95°C.

4.18. Integrated Operation of the Hydrogen Generator with PEMFC

The performance testing of the hydrogen generator coupled with PEMFC was carried out. The hydrogen generator described in the section 10 was connected to PEMFC through a series of traps and filters. The reason for that was that hydrogen produced in the hydrolyzer could carry a fine mist that could potentially damage the FC. Hydrogen stream passed through a glass wool filter and then humidifier to reach the desired level of relative humidity (RH). Fig. 27 depicts a single-cell PEMFC used in the experiments along with the testing station. PEM fuel cell with 5 cm² active membrane area assembled at FSEC was used in this task; it was connected to a Scribner 850C test station. The test stand operating at the same temperature as the fuel cell (80°C) served as a humidifier for the compressed H_2 and O_2 that were used during fuel cell conditioning (before the actual run with H_2 generator).

Fig. 27. A single-cell PEMFC and Scribner 850C testing station used in the experiments

For all the tests, the cell current density was controlled and cell voltage was recorded, with simultaneous measurement of cell resistance through high frequency resistance measurements. Each current density was held for 5 minutes to simulate steady state.

Fig. 28 shows the photo of the complete integrated experimental setup including $NaBH_4$ metering/delivery system (a syringe pump), H_2 generator, PEMFC and a test station (note that both H_2 generator and PEMFC were insulated by fiberglass, but for the clarity the insulators are not shown in the photo). PEMFC performance test using commercial high-purity H_2 from a tank was performed before and after the actual test using H_2 generated by the Al-$NaBH_4$ hydrolysis reactor. To accomplish that, the anode gas inlet to the fuel cell was connected to a three-way valve, which allowed for rapid switching between H_2 from a tank and from H_2 generator. The generated H_2 was humidified using a DI water-bubbler operating at about the same temperature as the reaction vessel (80-90°C), and all lines from the hydrolysis reactor to the PEMFC were heated and insulated to prevent water condensation. The cathode gas (O_2) from a tank was humidified to 75-80% RH, and the flow rate was held constant at all times.
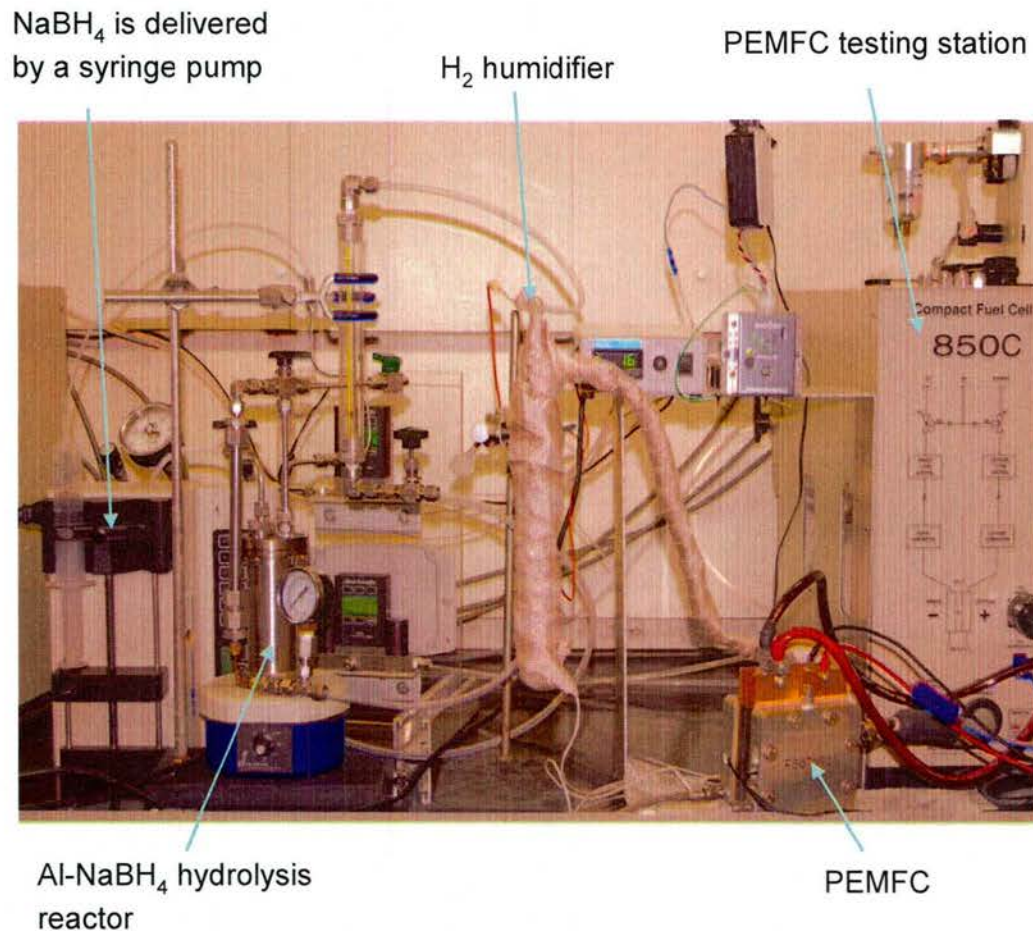
Fig. 28. Complete experimental setup consisting of NaBH$_4$ metering/delivery system, H$_2$ generator, PEMFC (shown without insulation) and FC testing station. Experimental conditions: hydrolysis reactor temperature T=92°C, pressure 1 atm. NaBH$_4$ stabilized dense solution (1:2 wt). Al- 20 μm powder. H$_2$ relative humidity 90%. PEMFC temperature 80°C

Fig. 29 shows the current-voltage curves for the performed tests. It can be seen that H$_2$ from the tank and from the H$_2$ generator give comparable results. This indicates that the activity of the cell is comparable with either source of H$_2$ gas.
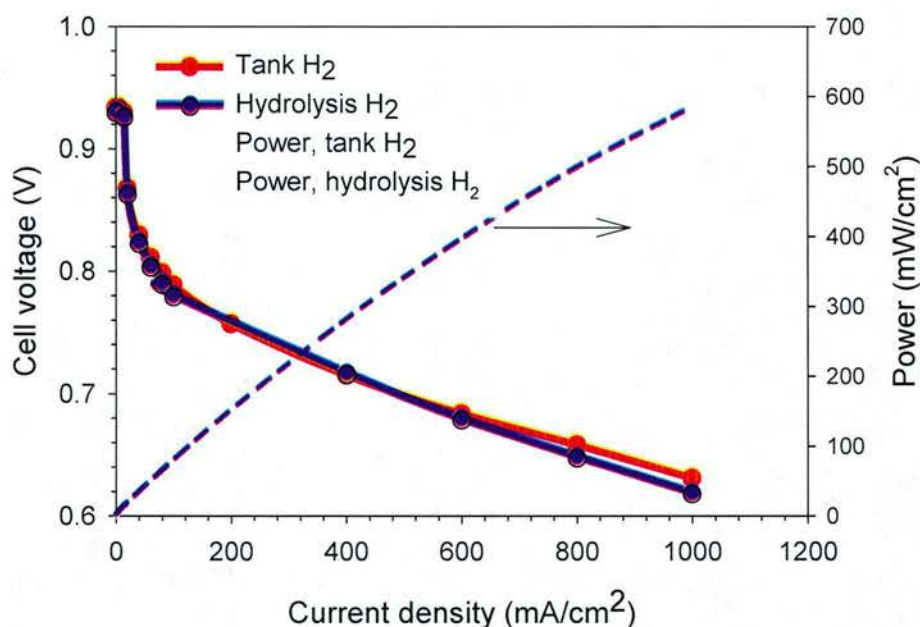
Fig. 29. PEMFC performance testing using H_2 generated by Al-NaBH$_4$
hydrolysis in comparison with tank H_2

The results of the PEMFC performance test showed that by using H_2 from the hydrogen generator the PEMFC produced about 0.6 W/cm^2 of power at current density of 1000 mA/cm^2, which corresponds to the total power output of the PEMFC of about 3 W (at membrane surface area of 5 cm^2). Taking into account the H_2 flow rate from the H_2 generator and H_2 utilization efficiency, the energy efficiency of the PEMFC was estimated at about 40-45%, which agrees with the values reported in the literature.

5. METHODS AND MATERIALS

5.1. Reagents

- H_2O: Water
  - Deionized (DI) water
  - Natural seawater (SW), 0.5 μm filtered, from Atlantic Ocean near Melbourne, FL.

- Aluminum:
  - Aluminum powder, West Systems Inc.- 99.7%, 50-60 μm
  - Aluminum powder, Fisher Scientific- 99.5%, 74 μm (200 mesh)
  - Aluminum powder, Sigma-Aldrich- 99$^+$%, 20 μm
  - Aluminum foil, Reynolds (degreased with acetone)

- NaBH$_4$: Sodium borohydride powder, purity 98$^+$% from Acros Organics

- NaOH: Sodium hydroxide, purity 99.99% from Sigma-Aldrich
- $CoCl_2 \cdot 6H_2O$: Cobalt (II) chloride hexahydrate, 98.6% from Fisher Scientific
- $FeCl_2 \cdot 4H_2O$: Iron (II) chloride tetrahydrate, 99% from Sigma-Aldrich
- NaCl: Sodium chloride
- α-Al_2O_3: Alpha alumina powder, 99% from Sigma-Aldrich, 10 µm
- γ-Al_2O_3: Gamma alumina whiskers, 99% from Sigma-Aldrich, 2-4 nm x 2800 nm long
- MgO: Magnesium oxide powder, 99.99% from Acros Organics
- TiO_2: Titanium (II) oxide powder, 99.9% from Sigma-Aldrich, $\leq$100 nm
- Bi_2O_3: Bismuth (III) oxide powder, 99.999% from Sigma-Aldrich

5.2. Experimental Setup

Experimental setups for each series of experiments are described in the corresponding sections of this report.

5.3. Experimental Margin of Error Measurements

In order to determine the experimental error of the H_2 generation system, several repeat experiments on Al-$NaBH_4$ hydrolysis were conducted in identical conditions. Figure 30 shows the 95% confidence margins for the synergistic reactions in this configuration.
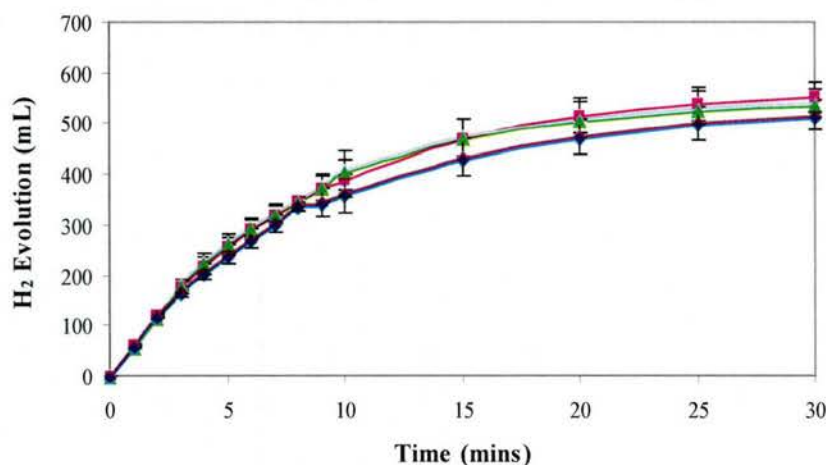

Fig. 30. Experimental margin of error in H_2 evolution measurements via Al-$NaBH_4$ hydrolysis

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